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U.S. and USSR MHD Electrode Materials Development

George Rudins

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DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

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PREFACE

This Report is part of a continuing Rand study, sponsored by the Defense Advanced Research Projects Agency, of selected areas of Soviet science and technology. It is based on comprehensive coverage of the Soviet literature exclusively in the public domain, as well as on exchanges between U.S. and Soviet specialists at international magnetohydrodynamic (MHD) conferences and meetings.

The present Report is the second of two dealing with Soviet MHD research and development. It provides an overview of developments in U.S. and USSR MHD materials research, perhaps the major problem area in MHD technology. The first Report, by the same author, *U.S. and Soviet MHD Technology: A Comparative Overview*, R-1404-ARPA, January 1974, treated U.S. and Soviet hardware developments, with special emphasis on open-cycle MHD, the area in which most of the Soviet effort appears to be concentrated.

SUMMARY

The USSR has had a large MHD materials-development program for a number of years. Many materials have been tried but with only limited success. The large MHD materials testbed facilities used in the Soviet program are unique and provide the USSR with an excellent capability for testing and evaluating promising candidate materials in a realistic commercial MHD environment. The U.S./USSR cooperative program on MHD will give U.S. researchers access to the latter facilities for materials-testing and channel operation purposes.

The United States has comparatively neglected MHD materials development, apparently because of the funding constraints imposed by the overall U.S. MHD program and because the early U.S. program emphasized short-duration systems and assigned only secondary priority to materials problems. While neither country's MHD materials research program has progressed sufficiently for a very precise assessment of the state of the art, the U.S. and USSR appear to be at about the same level.

The two national programs are now undergoing some change. In the last two years, the USSR has shown increased interest in new materials development -- refractory oxides and fiber-reinforced composites. U.S. researchers have proposed several new materials research directions. And this year, for the first time, the U.S. program has adequate funds available to initiate an integrated MHD materials development effort.

CONTENTS

I. MATERIALS PROBLEMS: DEFINITION AND REQUIREMENTS

It has frequently been stated that the success of open-cycle magneto-hydrodynamic (MHD) power systems will depend on the development of suitable materials that will withstand the harsh environment commonly found in coal-fired MHD systems. Much of the controversy on the best approach to MHD research and development in the United States centers on the need for an integrated R&D program where materials research is a major component versus concentration on the design and construction of facilities of ever greater size and complexity with a small, separate materials development effort.

From the viewpoint of open-cycle systems, materials certainly appear to be one of the two most serious problems impeding MHD development today; the other is the achievement of high enthalpy extraction. The materials problems within the generator duct itself -- e.g., the preservation of the structural and electrical integrity of the electrode and insulation modules -- are perhaps the most difficult.

Since the main thrust of the U.S. commercial MHD effort (and presumably the long-range Soviet effort as well) is for an open-cycle coal-fired system, the coal combustion products and the seeding compound will determine the chemical environment the MHD materials must withstand. High corrosion and degradation rates will occur unless protective measures are taken [1]. Interface reactions will cause new phases to form; seed-slag will flow over the electrode modules (however, preliminary Avco and University of Tennessee Space Institute [UTSI] experience has not found that this increases electrode wear); and electrode surfaces will be exposed to very high temperatures (which may result in excessive vaporization rates and preferential volatilization). Figure 1 shows the schematic recession rates as a function of temperature for seed, seed-slag, and vaporization regimes [2].

The most notable feature of the open-cycle coal-fired MHD generator is the presence of coal slag. The percentage, composition, and properties of slag and ash vary considerably from one coal to another. The ash content may range from less than 8 to more than 25 percent,
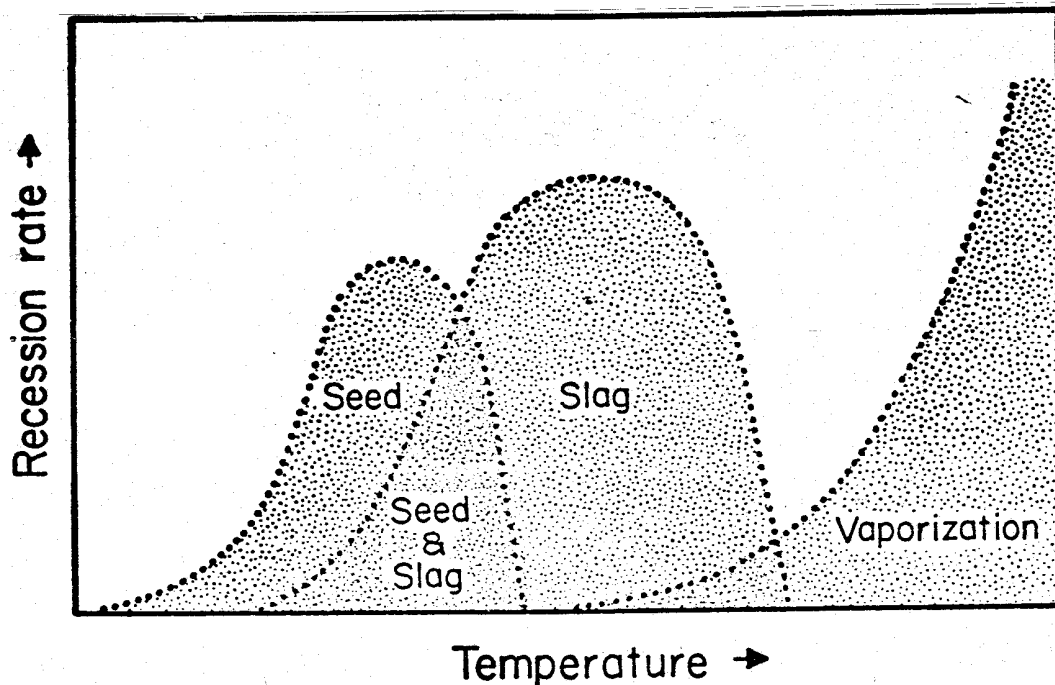
Fig. 1 -- Schematic electrode recession rates as a function of temperature
for seed, seed-slag and vaporization regimes [2]

about 10 percent being typical. The Bureau of Mines has published reports
on the composition and some of the characteristics of many U.S. coals [3].
It is presumed that at least 90 percent of the ash content of the coal
will be removed in the combustion process; if that can be achieved, the
problem should be fairly manageable.

The working generator environment in coal-fired systems consists of
high velocity hot gases (fossil-fuel combustion products and alkali metal
seed) with actual wall temperatures around 1500°C and 1700°C, depending on
the specific applications. The oxygen partial pressure of the gas mixture
is in the range of 10^{-4} to 10^{-2} atm. However, the gas is a mixture of N_2,
CO, CO_2, O_2, SO_2, NO_x, alkaline oxides, sulfates or carbonates, and coal
ashes (mainly silica).

MHD materials development programs have traditionally assigned high
priority to finding suitable electrodes, and most of the materials work
has been in this area. However, MHD materials specialists speculate
that finding good insulators might prove to be an even more difficult

problem. Insulators must have the same mechanical, chemical, and thermal stability as the electrodes while maintaining high electrical resistance (at least 100 times more resistive than the ionized gas phase and at least 10 times more resistive than conductors). For typical electrode/insulator design configurations there is an axial voltage of about 30 volts between electrodes, and therefore the dielectric strength of the insulator must be sufficient not to break down. Nevertheless, electrode development is generally conceded to be one of the first major hurdles in any MHD program. As a result (and because of a scarcity of literature on other materials problems), this Report will concentrate on U.S. and Soviet research on electrode materials.

Electrodes and insulators do not represent the only materials difficulties with which MHD designers and materials specialists must contend. The overall materials situation in MHD systems is twofold, divided between the MHD generator duct and the auxiliary components that constitute the system. Since the MHD generator is the heart of the system, the decision to proceed into complete system hardware can be made only after significant progress is achieved with the generator; it is therefore entirely appropriate to concentrate on channel materials problems at this stage. However, the design of such other components as the combustor, air-heater, and steam generator certainly cannot be viewed as being simple and straightforward from a materials point of view. The introduction of coal slag into the working environment, whatever potential benefits it may have for the MHD generator channel (and this issue is currently being debated in the U.S. research community), will lead to difficulties for all other components. At the moment, the available evidence for both Soviet and American programs suggests that the auxiliary components can be made to operate quite effectively on a clean fuel such as natural gas, but the clean fuel seems to have an adverse effect on the duct's operating conditions. U.S. studies (particularly those at UTSI) suggest that coal-slag can be put to advantageous use as a channel-wall lining material; but its predicted negative effects on other components may result in an overall system performance penalty.

Electrode problems have been historically associated only with corrosion, chemical reactivity with the gas plasma, unsuitable thermal

or electrical conductivity, or a combination of all three (see Figs. 2 and 3). There are at least two other considerations central to this question -- material compatibility and the interplay between system design and materials requirements. The latter two may prove to be more important than the former three.
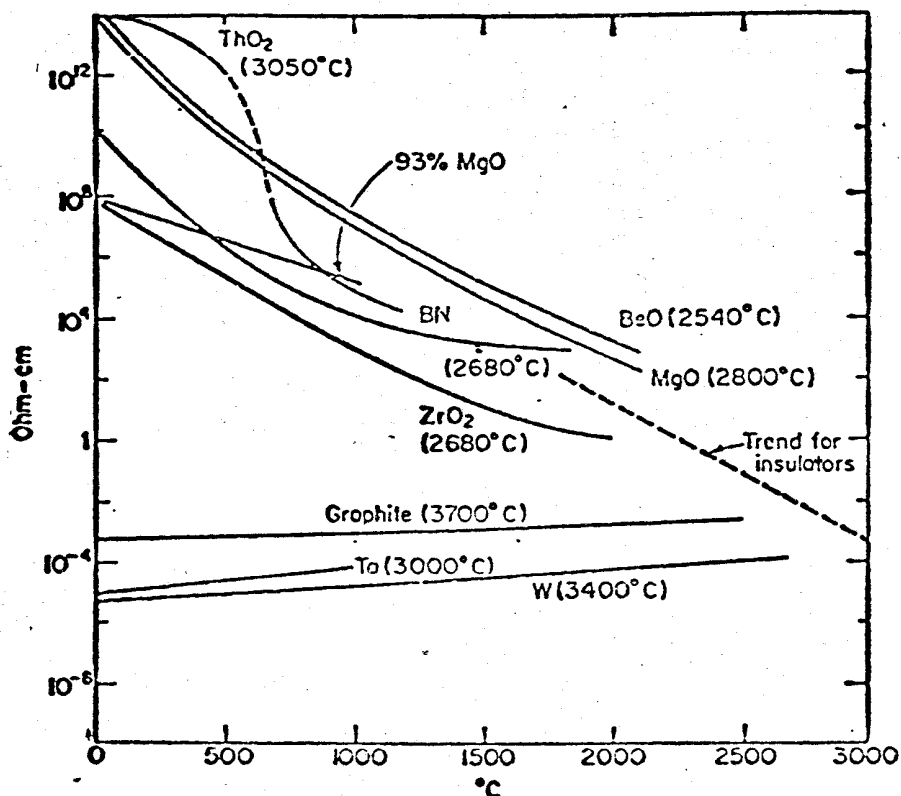

Fig. 2 -- Variation of resistivity with temperature of various materials [4]

A number of U.S. materials specialists believe that the composite nature of the MHD electrode module now under consideration, where one bulk material must interface with another, will pose a serious compatibility problem. The channel walls undergo thermal cycling and operate under very large thermal gradients; therefore, matching an electrode first with an insulating material, then with a metallic cup to hold it in place, and then with the cooling equipment and current leadouts is difficult. Furthermore, the electrode module itself must also be able to withstand
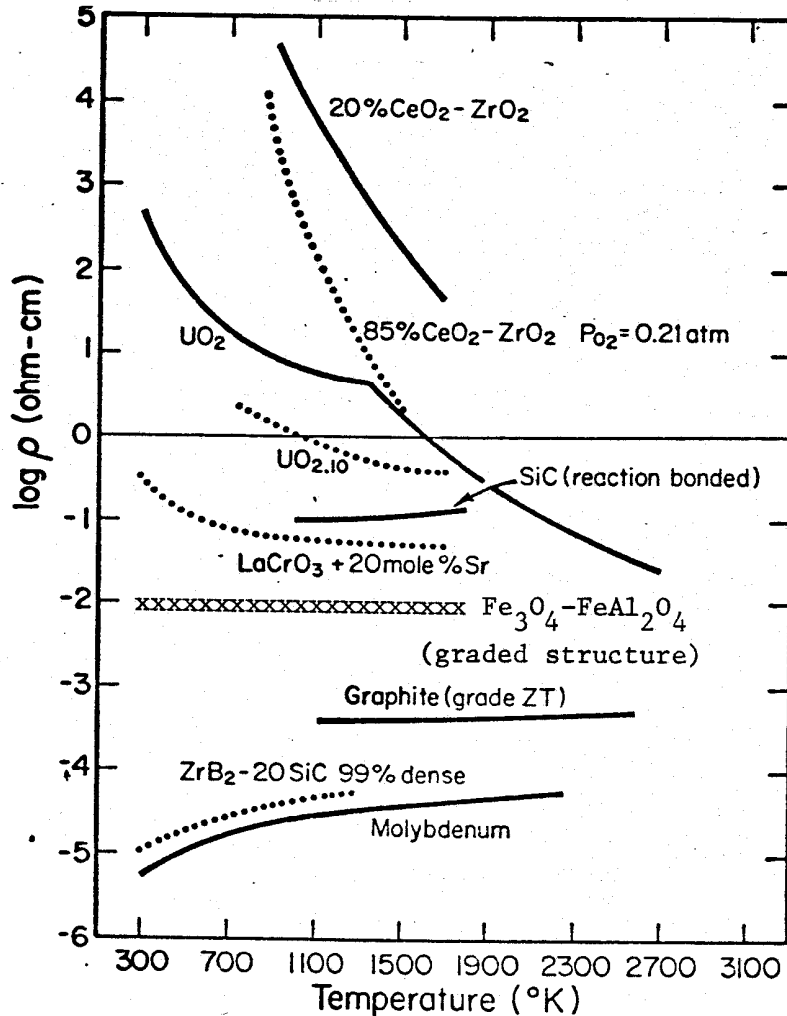
Fig. 3 -- Resistivity of candidate electrode materials
as a function of temperature [2,5]

a number of rather severe gradients near the electrode-slag-plasma
interface (see Fig. 4) [2]. Up to this time, little U.S. or Soviet
work on this materials compatibility problem is known.

While U.S. research has already shown that this may be a major
materials problem and that electrical effects within the generator
dominate materials performance long before chemical reactions affect
a material's structural properties, only by understanding the impli-
cations of the MHD environment and tailoring materials to meet the
needs can an MHD materials program succeed. Materials engineers and
system designers must cooperate so design positions and specifications
can be modified to everyone's satisfaction as experience is gained.
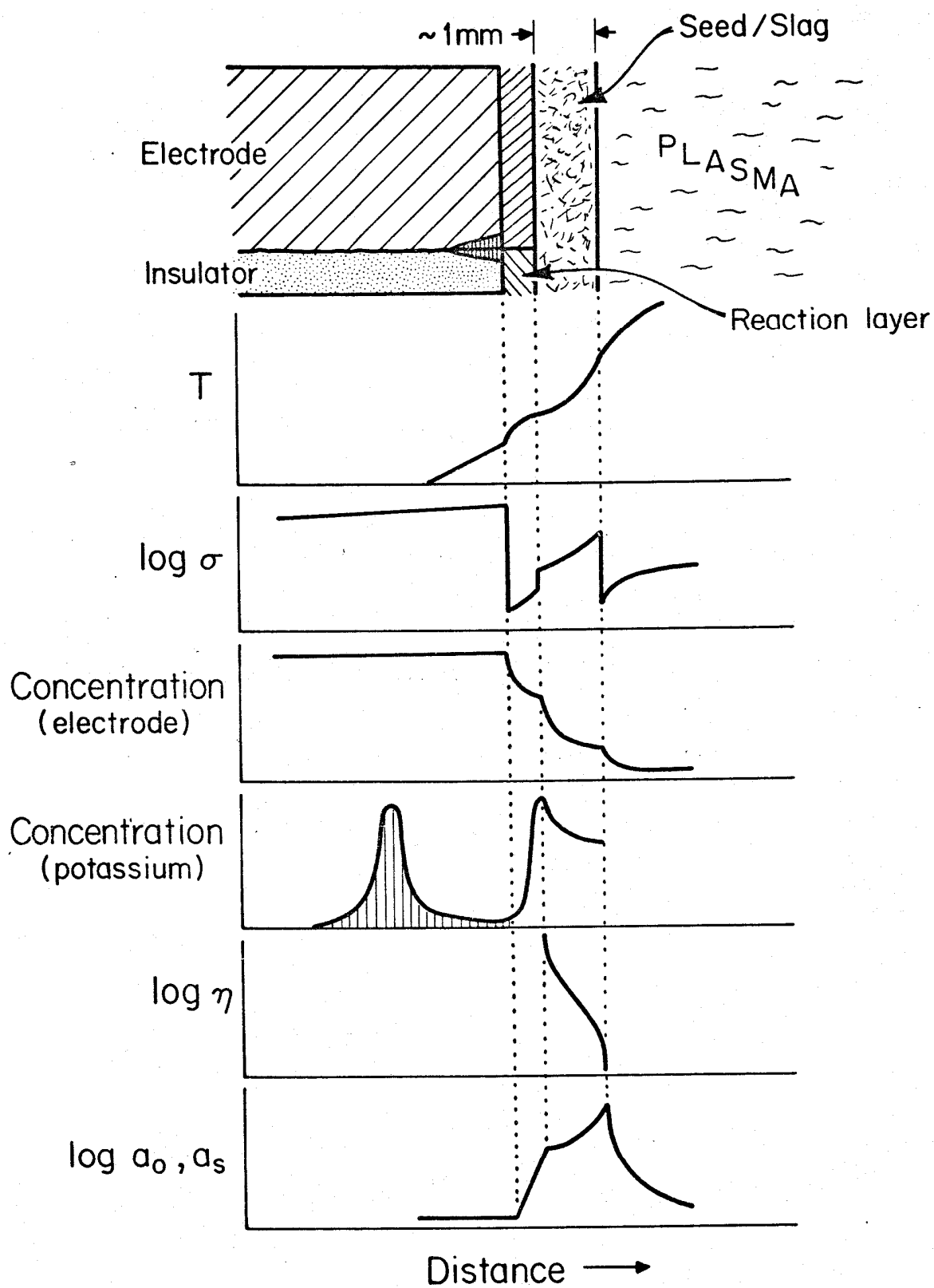Materials work should unquestionably be integrated into the overall

Fig. 4 -- Schematic of gradients near electrode-slag-plasma interfaces [2]

T - Temperature
σ - Conductivity
η - Viscosity

a_o - Oxygen Activity
a_s - Sulfur Activity

MHD R&D effort, for a great deal of time and effort can be wasted on exploring materials that appear to have the right thermal and mechanical properties only to find that they either do not sustain the electrical conditions found in an actual system environment or are not capable of being mounted in electrode-insulator systems, or both. MHD specialists contend that design, engineering, and fabrication constraints must be continually imposed on materials development. There is no other way to ensure that R&D resources will be applied efficiently to genuine engineering problems. This pragmatic approach is exemplified by industrial research and development aimed toward a high technology market product. Such work focuses sharply on cost or performance problems, whether associated with design, materials, or fabrication and usually a mix of all three.

In many instances an interplay of specialists can serve to reduce the severity of certain materials problems at the cost of perhaps further system complexity or some other tradeoff. The phenomena of interelectrode arcing and current concentration on the electrodes illustrate the point. The step function nature of the potential distribution in a segmented-electrode generator leads to the localization of arcing at the anode in the direction of higher potential with accompanying localized heating and subsequent rapid erosion of the electrode and adjacent insulating material. The erosion can be considerably reduced or perhaps eliminated by obtaining uniform current distribution on the electrode surface. This may be possible by: (1) designing asymmetric electrodes, (2) proper choice of electrode segmentation, (3) decreasing working fluid conductivity, (4) increasing the electrode-coating layer thickness, (5) using current conditioning hardware or "hot" electrodes (i.e., electrodes with surface temperatures of 1500°K and above). Hot electrodes tend to stabilize current transfer in the gas boundary layer and improve current distribution through thermionic emission. The latter design considerations can be manipulated by the system designer.

Current conditioning equipment adds undesirable complexities to the system, and the major drawback to the hot approach is the hostile materials environment characteristic of such designs. The hot wall approach would

probably be adopted universally if insulators and conductors of high quality and with good high temperature corrosion resistance were available.

Early hot electrodes were made of carbon, which worked well but was consumed very rapidly by the hot combustion products. Carbon's successor -- stabilized zirconia -- also tended to erode significantly with prolonged use, but U.S. researchers found that by introducing small amounts of zircon into the plasma stream the electrode could be replenished and its longevity increased.

Cold electrodes (<700°K) are usually considered to be water-cooled metals, such as copper, which have the advantages of being easy to fabricate and fairly unsusceptible to high-temperature problems but the disadvantage of being more subject to intense electrical arcing. They are therefore considered to be unacceptable for long duration MHD applications. Also, the thermal losses encountered in a cold wall duct introduce a small penalty in large generators.

At the present state of the art, some materials specialists contend that refractory oxides appear to be the most suitable materials for the various elements of the hot wall MHD generator, but it would probably be difficult to obtain general agreement on this point. Borides and carbides, once considered for electrodes, have long been in disfavor in the United States because of their poor oxidation resistance.

Refractory oxides appear to be particularly well suited for MHD materials because their low oxidizability minimizes deterioration through oxidation; however, refractory oxides are particularly susceptible to thermal shock failure, with which the Soviets appear to be having considerable problems. This weakness may perhaps be overcome by increasing the oxide's porosity; however, this approach greatly reduces the oxide's resistance to slag penetration and accompanying deterioration.

Unfortunately, none of the studied materials in the United States or Soviet Union meet all of the requirements deemed necessary by a group of experts convened by the U.S. Office of Coal Research (OCR) and outlined in Table 1. The best candidate materials at present -- silicon carbide,

lanthanum chromite, zirconia, and zirconium diboride -- cannot do the job when subjected to continuous long-duration operation. Table 2 lists their basic parameters, which have been measured or estimated from available data.

Table 1

REQUIREMENTS FOR MHD ELECTRODE MATERIALS

Requirement	Remarks
Conductivity – electronic	Conductivity $\approx 10\Omega cm$; flux ≈ 1 amp/cm^2, temperature dependence
Corrosion resistance	Potassium seed, aluminosilicate slag (with iron, sulfur, etc. impurities) of varying composition
Erosion resistance	High velocity gases and particulates, and flowing slag layer
Good thermionic (electron) emission	The anode and cathode should be good acceptors and emitters, respectively
Good thermal conductivity	High heat flux from the hot plasma (2500°C)
Oxidation (reduction) resistance	The effective oxygen partial pressure in the duct is about 10^{-2} atm
Thermal shock resistance	Significant thermal shock problems in start-up and cool-down
Compatibility	Insulator, cooling coils, metal electrical leads, etc.
Mechanical stability	Creep resistance
Ease of fabrication	
Cost	

Table 2

PROPERTIES OF PROPOSED ELECTRODE MATERIALS [1]

	SiC	(LaSr)CrO$_3$	Mo	ZrO$_2$ + CeO$_2$	ZrB$_2$ + SiC
Resistivity (ohm·cm)					
1000°C	0.11	0.10	32 x 10^{-6}	1.48 x 10^3	54.5 x 10^{-6}
1200°C	0.14	0.10	37 x 10^{-6}	2.64 x 10^2	66.0 x 10^{-6}
1500°C	0.18	0.10	48 x 10^{-6}	3.16 x 10^1	79.5 x 10^{-6}
Strength [(dynes/cm^2) x 10^7]	124 (98% dense, T=1500°C, flexural strength)	31.0 (Bend strength at room temperature)	69 (Tensile strength T=1300°C)	--	345 (100% dense, T=1000°C)
Young's Modulus [(dynes/cm^2) x 10^{10}]	340 (98% dense, T=1500°C)	--	145 (T=1300°C)	67.6 (15 mole % CeO$_2$, room temperature)	476 (100% dense, T=1000°C)
Thermal Expansion Coefficient x 10^{-6}	5.9	10	11.1	12.5	7.63
Vaporization rate at 1500°C (g/cm^2·sec)	2.5 x 10^{-8} Po$_2$ = 10^{-2} (calculated maximum)	3.0 x 10^{-7} Po$_2$ = 0.25	--	--	4.5 x 10^{-6} Po$_2$ = 0.3
Oxidation rate in air measured by weight gain (g/cm^2·sec)	-2.1 x 10^{-10} (after initial 20-hr period, T=1100°C)	Loss of Cr at rate of 6.3 x 10^{-5} g/g/hr, Po$_2$ = 10^{-2}	Severe	Negligible	5.7 x 10^{-9} at (T=1000°C after initial 2-hr reaction period)
Dissolution rate in unsaturated coal slag [(cm/sec) x 10^{-6}, T=1450°C]	100 (for SiO$_2$ in calcium-aluminum-silicate slag, T=1500°C)	2.47	2.55	2.65 (for CaO-ZrO$_2$)	0.236 (for ZrB$_2$ alone)

II. HISTORY AND ORGANIZATION OF NATIONAL EFFORTS

The early impetus for MHD power generation was provided by the United States, which was rapidly followed by Britain, France, Japan, USSR, Poland, and West Germany. The British effort was directed to the construction of a prototype plant, and they had a well-integrated program. The British program emphasized the actual use of materials in the MHD system and included much of the original work on lanthanum chromite systems. This program also first identified the problems of current channeling and electrolysis in the zirconia-based compounds stabilized with calcia and yttria. However, the British work was halted in 1967 for economic reasons. At that time nuclear power in Britain had become cheaper than the cost predicted for MHD power, and the British assumed that the fast breeder reactor would definitely be operational by 1980 (thereby sharply curtailing the need for fossil-fuel power plants).

A review of the various national programs in operation during the 1960s makes it clear that although the British program was the most integrated, especially since it included the use of coal, the French program was the most comprehensive in regard to materials evaluation (see, for example, Yerouchalmi's overview of selected French work on materials [6]). This was perhaps because the French effort included the outstanding high temperature materials groups around Paris at a very early stage. These studies involved high temperature measurements of zirconia-based compounds, including most of the dopants examined later by the Soviets, and the fabrication of high temperature insulators (including the very resistive zirconates). Comparison of Soviet and French literature on MHD materials suggests considerable French influence on the Soviet program (perhaps as a result of Soviet-French cooperation in the sciences).

The United States, Britain, France, and West Germany did have the most notable early MHD efforts, but the programs of the last three have been effectively terminated in recent years, with the banner passing to

the Japanese and Soviets. The Japanese have been particularly success-
ful in the early 1970s, but they apparently have not decided whether to
design and construct an MHD installation in the near future.

The most impressive MHD effort now underway is in the USSR. It
represents a well-integrated program centered at their Institute of
High Temperatures. The program is unique in that the Soviets have
tremendous supplies of clean fuel (natural gas) to burn in their
facilities. Although the USSR apparently rationalized using clean
fuel for its pilot plant experiments to reduce materials and other
systems problems,* they may have actually considerably intensified the
electrode wear problem over what it would have been if coal were used
(if the preliminary UTSI and Avco findings mentioned earlier bear out).

Whether the final goal of the Soviet program, from its inception,
was the development of coal-fired plants or clean-fuel systems has little
bearing on their current effort. The Soviet program is now very much
committed to completing the current work on gas-fired plants and deter-
mining whether it will be appropriate to go ahead with the construction
of a 1,000 megawatt gas-fired prototype plant. There is visible Soviet
interest in coal, but it is building up slowly; it will probably be
several years before a coal program is firmly established. The world-
wide research effort in MHD generator technology and the nature of the
Soviet program are discussed in greater detail in a recent Rand Corpora-
tion Report [7].

The energy shortage renewed U.S. interest in MHD energy conversion,
which is evident in the much higher government funding levels for com-
mercial MHD in FY 1975 (about $13 million). More monies have also been
allocated to materials research. Still higher funding levels are ex-
pected in subsequent years. The estimated cost of the national MHD

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*In the presence of clean gases, electrode protective conditions
can be obtained by supersaturating the clean combustion products with
the ceramic material used in the electrode. The protection of high
temperature electrodes in the presence of coal combustion products
requires controlling the properties of the slag layer covering the
electrode surface [1].

program proposed by OCR and the Electric Power Research Institute (EPRI) is $154 million for the period FY 1975-1979, with an additional projected cost of $175 million for the period FY 1980-1984 [8]. The newly formed Energy Research and Development Agency (ERDA) will bear the responsibility for leading the national effort. The major short term objective of the program is to complete the design, fabrication, and checkout of a 50-100 megawatt thermal Component Test and Integration Facility (CTIF) and to initiate testing in this facility by the end of FY 1979 for both clean and sulfur- and ash-laden fuel sources. The longer term objective is to complete design, fabrication, and checkout and to initiate testing of a 250-500 megawatt thermal Engineering Demonstration Plant (EDP) [8].

The Soviet MHD program enjoys a very high priority in the USSR, and integrated plant experience and materials development are being particularly stressed. The Soviets have dozens of research institutes doing work on materials (see the Appendix), but there appears to be little central coordination of their activities; duplication of effort seems to occur frequently. A great deal of work is going on in the development of corrosion-resistant refractories that is not picked up in the Soviet MHD literature. Soviet materials journals such as *Ogenupory* only occasionally mention work specifically directed toward MHD; yet they have numerous pertinent articles.

There is, however, a clearly definable, cohesive MHD materials effort centered on the Soviet Institute of High Temperatures (IHT), with visible input from a number of other Soviet research institutes -- e.g., the USSR Academy of Sciences' Institute of Physics (refractory oxides), Moscow State University's Institute of Mechanics (numerical analysis), the Volgograd Polytechnic Institute (explosive compaction techniques), the USSR Academy of Sciences Baykov Institute of Metallurgy (spheroid-powder oxides), and UNIIO Ukrainian Scientific Research Institute (refractory cements) [9].

The IHT is very much oriented toward materials development and characterization. Much of the work involves testing and further development or use of materials first developed in other institutes, but there are, apparently, in-house materials development programs as well [9].

The IHT employs more than 2,500 people, about 1,000 of whom carry out physical research. Most of these people are probably technicians, but the 1974 IHT annual report does state that at least 188 have advanced academic degrees equivalent to the U.S. Ph.D. or higher -- six full members of the USSR Academy of Sciences, two corresponding members, 24 with the doctor degree (roughly equivalent to full professors), and 156 candidates of science (roughly equivalent to Ph.D.s) [9]. The Institute of High Temperatures has few theoreticians, but the Soviets have stated that they receive theoretical backup from institutes concerned more directly with materials.

With the on-again, off-again MHD programs in the United States during the 1960s, the military was the principal sponsor. By the end of the 1960s the Soviet program had advanced and U.S. energy problems had become critical enough in 1968 to make the Office of Science and Technology (OST) form an MHD panel to evaluate the potential of MHD power generation. In its recommendations [10] the panel confirmed the soundness of the concepts of MHD but indicated that with coal-fired systems, considerable government support would be required to build the demonstration facility. Following the recommendations of the OST panel, a task force on MHD was formed by representatives of public and private utilities and of government agencies. In this regard, in 1971 the Office of Coal Research (OCR) asked MIT to provide an assessment of the technology for MHD power generation and to propose a systematic program for its development [11]. This apparently was the first time that a national program had considered all facets of MHD power generation. In particular, the report recommended a materials program over ten years that involved about 10 percent of the total funding for the overall national program. It consisted of immediate materials work for the generator, air-preheater, and auxiliary equipment, and a technology demonstration phase. The support technology phase included a rigorous study of slag properties and materials for electrodes, insulators, and refractories as well as corrosion studies, development of fabrication techniques, and studies of integral parts.

The MIT report was not well received by all MHD investigators. In the United States it was not generally accepted at that time that significant materials development would be required in order to operate an MHD generator for any length of time. The report was, however, accepted by the Office of Coal Research and the Utilities Electric Research Council as a working document. In 1972, additional presentations were made to the Director of the Office of Coal Research. However, the proposed plan was never implemented; monies continued to be spent to build generators at UTSI, Westinghouse, Avco, and Stanford, but little was done to develop research programs for materials. The United States was then constructing four generators and not stressing centrally organized backup technology. Each of the laboratories wanted to have its own long-duration test facility. As problems began to arise at these facilities, they began to consider a small amount of in-house materials research; e.g., Avco-Everett began doing some materials corrosion work. The University of Tennessee Space Institute also began to recognize materials problems and tried to develop its own materials efforts.

During this period, the National Science Foundation, through their RANN Division, decided to fund materials work for MHD and started off with a program of about $75,000 per year at the University of Utah for corrosion and thermionic-emission studies. The following year OCR established a materials coordination committee to meet in conjunction with the quarterly program review meetings of all of the OCR contractors. Small materials efforts were established at the generator facilities -- e.g., Westinghouse Research Laboratories began materials research at about a one-half man-year rate, using a high-temperature test-facility to test electrode materials at temperatures greater than 1700°C. An ad hoc working group was also set up in conjunction with the U.S./USSR program for materials tests, especially those in the U-02 facility.

The program that has apparently given the most emphasis to the establishment of significant U.S. materials efforts for MHD generators was the recently negotiated joint program with the USSR. At the end of

the initial two week visit to the USSR many of the participants exhibited greater interest in testing materials at their facilities -- e.g., Avco showed increased interest in testing materials in demonstrating the feasibility of electrode coating. UTSI offered to make their facility available for testing of newly developed materials for electrodes and insulators. The STD Research Company in California, which had been mainly involved with computer studies and plasma dynamics, set up a facility to test materials.

A centrally organized national program for the development of MHD materials is now evolving and the situation will probably improve as more money becomes available. Already, a draft for a new overall program for the development of MHD power generation has been completed. It places considerable emphasis on materials development [8]. That program outline was prepared jointly by the Electric Power Research Institute and the U.S. Office of Coal Research. Also, an engineering workshop on MHD materials was convened at MIT in November 1974 under the auspices of the NSF and OCR for the purpose of:

1. identifying critical materials problems that require solution in order to further MHD technology over the near and long terms, and assessing current capabilities or new procedures for solving these problems.
2. imparting information being developed under current research and development programs in MHD materials being sponsored by NSF and OCR to interested representatives of industry, national laboratories, not-for-profit institutes, and the academic community; and
3. involving the engineering community in identifying where there have been successes in the development of materials and design information for MHD applications and where efforts should be directed to translating these successes to first-generation MHD system reality.

The U.S. materials program, as it now stands, consists of eight projects at eight facilities.

1. Westinghouse: Westinghouse has a one-half man-year effort
    for MHD materials concerned mainly with the development of
    electrodes that will operate above the slag condensation
    temperature and is now leading the Phase I effort on ma-
    terials testing at the Soviet U-02 facility.

2. Avco-Everett: Some corrosion experiments with respect to
    sulphate degradation of refractories for heat-storage ma-
    terials have been carried out, but this is a minimal effort.

3. UTSI: Tests are being run on the UTSI facility to test
    electrodes and insulators to determine corrosion rates and
    to study phase changes that occur during channel operation.
    Studies are also being set up specifically for materials
    development.

4. STD Research: They have initiated some studies on the inter-
    action of plasma with electrodes; but again, it is a very small
    effort.

5. University of Utah: The University of Utah has about $75,000
    per year from the National Science Foundation. The effort
    focuses mainly on the corrosion of refractories for the pre-
    heaters and the high-temperature electrical and electron-
    emission properties of electrodes. The work is now at a point
    where significant results are being generated.

6. National Bureau of Standards: The program at NBS has grown
    from the initial $12,000 per year to approximately $250,000.
    The program focuses on the analysis of high-temperature prop-
    erties of slag, including electrical conduction and viscosity;
    examination of the phase relationships with respect to sulphates
    and refractory silicates; and studies on high-temperature elec-
    trical conductors. The fundamental work at NBS is important to
    the developmental programs that will probably eventually be
    funded by the Office of Coal Research.

7. Battelle Northwest: Battelle is involved in the Soviet coopera-
    tive program, in which capacity they are characterizing the
    high-temperature electrode materials (at about $100,000 per
    year).

8. <u>MIT</u>: The initial funds at MIT were spent mainly in a consulting relationship with the Office of Coal Research helping them analyze and initiate materials programs. The research effort for this year is at the rate of about $90,000 per year for direct materials work.

In addition, the United States has recently agreed on a cooperative program on MHD with the USSR, and several millions of dollars have been set aside by the Office of Coal Research for this program. Although the details are not yet precisely worked out, the program will consist of construction of MHD ducts and auxiliary facilities, which will be studied at the existing Soviet facilities. Eventually there will be some Soviet studies on U.S. ducts. In the planned joint materials program, outlined in Table 3, the Soviets will make their U-02 facility available to U.S. researchers for materials studies.

Table 3

U.S./USSR JOINT U-02 MATERIALS PROGRAM

Phase I (first quarter, FY 1975)	Conduct a 100-hr. test of ZrO_2-based solid electrodes under current U-02 operating conditions

Proposed

Phase II (third and fourth quarters, CY 1975)	Conduct a 100-hr. test of modifed ZrO_2-based, ZrB_2, and SiC electrodes under current U-02 operating conditions
Phase III (first quarter, CY 1976)	Modify U-02 facility to operate under K_2SO_4 and K_2CO_3-K_2SO_4 seeds
Phase IV (second quarter, CY 1976)	Conduct a 100-hr. test with K_2SO_4 seed and coal slag injection in the U-02 facility
Phase V (fourth quarter, CY 1976)	Conduct a 1000-hr. test with K_2SO_4 seed and coal slag injection in the U-02 facility

III. DEVELOPMENT APPROACHES

The USSR has had a very large, broad-spectrum MHD program for a number of years, with very few aspects of MHD being ignored. The open-cycle effort has concentrated on natural-gas fired systems. The program has achieved some successes, notably the construction of a large-scale, open-cycle MHD pilot plant (the U-25), which has also served as a very useful testbed for materials testing under realistic conditions.

The U.S. program, partly by design but also partly because of Department of Defense applications interests, developed MHD generators on a high-power, short-time basis and utilized small facilities for the selection and limited testing of a few candidate materials (the so-called two-axis approach). However, the Soviet program concentrated directly on pilot-plant development. The Soviets reasoned that a small installation involving all of the components of an MHD system should first be operated both to test materials on a long-duration basis and to determine the problems of interconnecting the various components. As a first step, the Soviet Union chose to construct a small scale model of a complete MHD pilot plant (the U-02) and to concentrate on the integrated operation of such a plant. This approach had an important limitation. It did not allow the Soviets separate control of the experimental parameters of each of the major components for the purpose of component optimization, nor did it provide the experience of significant MHD effects in generator ducts. It did, however, give a great deal of data on a large number and variety of materials under the specific U-02 and U-25 pilot plant conditions. Although none of these materials is known to have been successfully operated for long periods in the MHD duct, the Soviet research data are still very useful.

The quest for suitable MHD materials has played a major role in the Soviet MHD development program, but the United States has never really had what might be termed an organized MHD materials development program on a national level. Various generator development programs

involved some materials research, but not as the focal point of such efforts, apparently because of a lack of sufficient funding and emphasis on short-duration operation. The overriding U.S. approach appears to have been, "buy it off the shelf on the basis of the materials supplier's recommendations."

The USSR has been stressing MHD materials development for a number of years and has been using at least three MHD facilities -- Start, U-02, and U-25 -- for extensive materials testing in a well-organized manner. The small Start facility (along with other small facilities) and the larger U-02 have served as testbeds and screeners for promising new materials. Favorable test results in a small facility apparently automatically send the material on to the U-02 for further testing. If the latter tests are favorable, the material goes on to the U-25 (pilot plant) for final testing, where it is exposed to an environment approaching that expected to be found in commercial scale facilities [7].

The U-25 has already served as a testbed for both hot and cold electrodes made of copper, various heat-resistant alloys, zirconia, lanthanum chromite, silicon carbide, composite materials, and others [12-16]. The United States has never had a single MHD facility that could be termed a materials testbed.

As in other fields of science, the Soviets have again shown preference for the "shotgun" approach to materials development. They have identified the categories of materials that might be appropriate to MHD and subsequently have methodically studied the materials in each category. Partial success with any one material apparently never diminished the efforts with other materials. As a result, although the Soviets have not revealed any materials unknown in the United States, they have gathered more information on existing materials than their U.S. counterparts.

The contrasting, typically U.S. "spiked" research approach can be seen in the MHD materials field. For example, early success with stabilized zirconia in electrode applications at Avco led to greater concentration on this material at Avco (and reduced interest in other materials), resulting in the development of techniques for furthering

zirconia's longevity in the MHD environment -- e.g., electrode replenishment and coating.

The latter research underscores yet another dissimilarity in the two countries' approaches. The Soviets have been trying to develop a permanent electrode by seeking a material that can survive about 1,000 or more hours of continuous operation without serious degradation, while the United States has concentrated on developing techniques for furthering the useful lifetime of existing materials.

EARLY WORK

In the early stages of electrode materials development, it was believed that cold (water-cooled) metallic electrodes could be used in MHD generators. However, U.S. studies showed that this led to the formation of a cool electrode boundary layer (with attending large electrode voltage drops and arc spots) and generally caused poor electrical performance. As a result, cold materials fell into disfavor in the United States. The approach did have the advantage of permitting the use of such metals as copper, but with accompanying erosion problems. In the corrosive medium formed by the combustion products and seed, ordinary metals can operate at only moderate temperatures, about one-fifth to one-eighth the temperature in the core of the plasma flow, where the conductivity of the plasma is practically zero and the current can pass to the electrode only by virtue of the electrical breakdown of the cold part of the boundary layer, with the formation of microscopic arcs. The formation of these arcs was found to cause a great increase in the erosion of the electrode [17]. The latter, however, applies primarily to high current density systems.

The early Soviet position on electrode erosion was that it was by no means always serious: It depended on the behavior of the arc and was ultimately determined by the properties of the material and the operating conditions of the electrode [18]. As a result, early Soviet work emphasized "cold" material technology. In 1967 the Soviets reorganized the U-02 facility into a materials testbed. Major emphasis was placed on "cold" MHD materials also because of the then current plans to build a much larger facility (the U-25) initially using such materials [19].

Initial Soviet studies using flat electrodes failed, primarily because of localized destructive arcing [20]. They then turned their attention to a wide range of other materials and electrode configurations and geometries, achieving their greatest early success with protruding hemispherical electrodes (Fig. 5); interesting results pertaining to boundary layer problems were also obtained with wing-shaped electrodes [18].
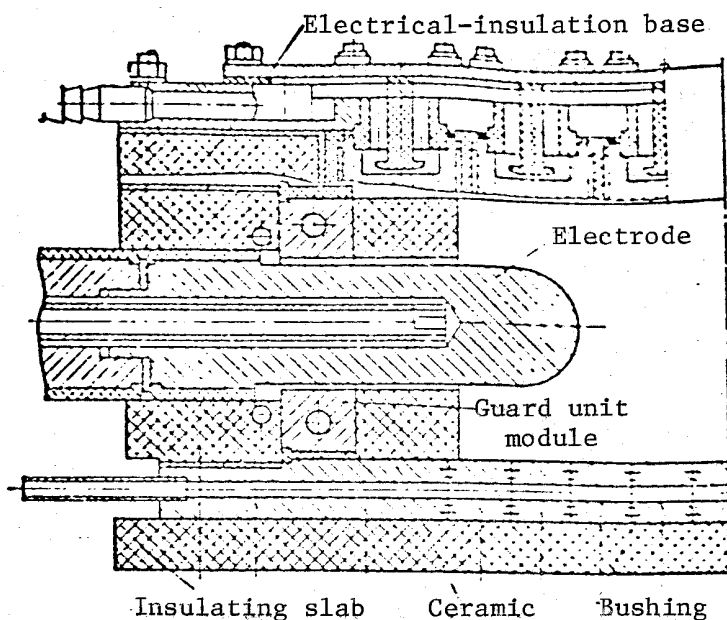

Fig. 5 -- Section of the channel with hemispherical electrodes [18]

According to the Soviets their first experiments with hemispherical electrodes showed no formation of destructive arcs. They observed more arcs with shorter lifetime and lower intensity than those found with plane electrodes. High-speed photography (up to 10^5 frames/sec) with synchronous oscillograph recording of the electrical parameters confirmed the main characteristic of the microscopic arcs (number, size, lifetime, and so on) in relation to the temperature, electrode material, and mode of operation [18].

In plane electrodes, the behavior of the arc is severely influenced by the concentration of the electric field at the leading edges of the

electrode. The Soviets reported that, in contrast, the behavior of the microscopic arcs incident on the hemispherical electrodes projecting into the flow was mainly determined by the gas-dynamic characteristics in the flow around the electrode surface. After the breakdown of the boundary layer, the flow carried away the tail of the arc, and a secondary breakdown occurred between the tail and the electrode surface in a new location. Since the region of breakdown was extremely narrow, the removal of the tail was determined not so much by the velocity of the incident flow as by the velocity gradient at the wall. In the region corresponding to the detachment of the boundary layer, at which the velocity gradient is almost zero, the arcs lost their mobility and were stabilized; their motion in this region depended on large-scale fluctuations in the flow [18]. Later studies in the U-25, however, apparently did not support these early findings, for the Soviets have published very little on the subject since.

CURRENT RESEARCH

The Soviets have reported being disappointed with the hemispherical electrodes in the U-25 and have apparently now turned their primary attention to plane electrodes. However, they have not totally abandoned research on either cold copper electrodes or hemispherical electrodes; both are still being studied in the U-02 facility [9]. The Soviets have also reported that they still consider the shape, construction, and design of the ceramic electrode material critical, particularly when one is considering thermal shock.

U.S. channel designers, over the years, have perhaps underestimated thermal shock problems from a materials viewpoint. The Soviets, however, have shown great concern for they believe that very large thermal gradients and nonlinear temperature profiles may be encountered that would severely restrict the candidate materials.

Some U.S. material scientists have formed the impression that the Soviets have been obtaining very good results with materials in laboratory tests, but not in actual runs in their test facilities. They believe that perhaps extreme thermal gradients and temperature fluctuations caused these materials to disintegrate completely. Some U.S.

channel designers believe that a more likely explanation of the poor performance in the actual runs is that the Soviets failed to realize the importance of electrical conditions in a situation where electrical effects dominate, not because of the fundamental limits of the material but because of the improper design of the system as a whole.

Current U.S. and Soviet work on MHD electrode materials reflects the early concentration in the respective MHD development programs. Much of the U.S. effort was for many years devoted to the development of generators for military applications, particularly the projects at Avco, where the emphasis was on attaining high performance. The military preoccupation with performance and their low interest in long duration operation apparently caused military-funded programs to assign a secondary priority to system longevity and the accompanying materials problems, but they nevertheless did generate a significant amount of information on a number of MHD materials. Non-military funds for MHD were very scarce until about 1970 (the Office of Coal Research was the main source of outside funding beginning in 1971) and program priorities always seemed to be such that new materials development was near the bottom of the list.

IV. MATERIALS INVESTIGATED IN THE SOVIET PROGRAM

The Soviets have published considerable literature pertaining to their work on MHD materials. Much of the information, however, has been fragmentary and incomplete. Specification of the precise test conditions, for example, is frequently inadequate, and occasionally some pertinent parameters are not even discussed. For this reason, some of the data presented in this section may appear incomplete, but it is the best available at this time. When the published Soviet data are correlated with U.S. experience in the field, there is usually sufficient information to evaluate the significance of reported developments.

The USSR has gained broad experience with a great number of materials under extreme MHD conditions. The carbides have been especially popular in the Soviet program, particularly silicon carbide [14,21-26] (but unfortunately with the final result that it could not last more than tens of hours [22]). Other carbides that have been recently emphasized in Soviet research are niobium carbide [27], zirconium carbide [28], boron carbide [29], tantalum carbide [30], carbide fibers [31], and solid solutions of titanium carbonitrides [32]. Other materials considered by the USSR from time to time to be promising for MHD applications are the periclase ceramics [22,26,33,34] (as insulators), boron oxide [35], and thorium and beryllium oxides [36]. The last two oxides have been studied by the U.S. and Japanese and have been rejected as far too costly and toxic (without sufficiently advantageous properties).

Of the new MHD electrode materials currently under study in the USSR, lanthanum chromite, lanthanum hexaboride, and fiber reinforced composites are the most recent. The Soviets have also reported some success in using explosive-compaction techniques for fabricating refractory cermets [9]. They found that some cermets prepared in this fashion and subsequently heat treated in the presence of argon at 1200°C show a five-fold reduction in their oxidation rate. Research on fiber composites specifically for MHD applications was initiated in the USSR in 1972 [13] and no hard data have as yet been published. The Soviets have reported only that their work with magnesia-fiber-reinforced magnesia showed a ten-fold improvement in thermal

stability at temperatures of 1300°-1500°C (compared with conventional magnesia) and a 25 percent improvement in durability. In studying SiC reinforced with single-crystal SiC fibers, they found they could obtain a 30 percent to 50 percent improvement in the material's durability (over that attainable with standard SiC). No information is available on their reported work with zirconia reinforced with single-crystal zirconia fibers. Research on LaB_6 was begun only in 1973 and there are no results yet available; the material is being studied from the viewpoint of using it in porous, gas-cooled electrode applications [9].

ADVANCED MATERIALS

$LaCrO_3$-Cr electrodes were reported to be nearly unscathed after 5-1/2 hours of operation in the Soviet U-25 facility, but the Soviets are apparently considering using the material mainly for current lead-outs [13]. While the use of lanthanum chromite for MHD has been considered for a number of years worldwide [37-46], its early development for such applications was hindered by the low funding of MHD programs (mainly in the United States), the unavailability of necessary fabrication techniques (mainly in the USSR), and the concentration of attention on other materials (zirconia in the United States and silicon carbide and cold electrodes in the Soviet Union). Soviet work on zirconia, although it has been considerable [13-15,22,25,26,27-61], appears to lag that of the United States in terms of results; in a number of instances published Soviet studies have simply confirmed U.S., French, and English findings [15]. Their zirconia research, however, has recently taken a new innovative direction -- investigation of zirconia-fiber-reinforced zirconia.

Increased Soviet interest in lanthanum chromite was apparently spurred by the Soviet success in developing an improved method for preparing lanthanum chromite and fabricating cermets based on it [13,62], as well as by the lack of significant progress with "conventional" materials [12-18,19]. $LaCrO_3$ is particularly attractive for MHD electrode applications because of its electronic conductivity, high melting point (~ 2500°C), low electrical resistivity over a wide temperature range, and

good oxidation resistance when doped or alloyed with suitable materials. (Figure 6 shows the temperature-resistivity curves for a number of LaCrO₃-Cr cermets examined by the Soviets [14].) The Soviets have emphasized work with chromium doping, while the United States (which only recently began studying lanthanum chromite for MHD applications [43-45]) has focused on doping with SrO.
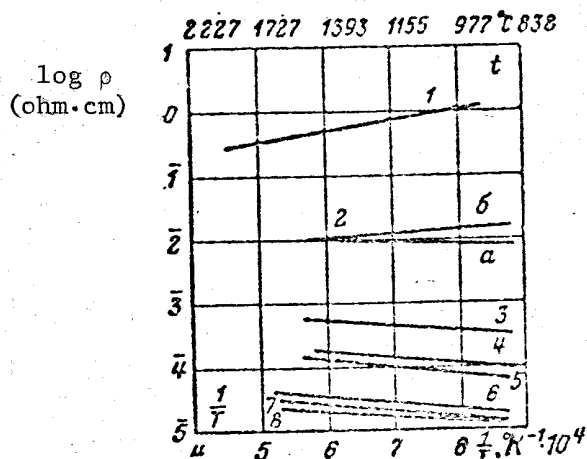

Fig. 6 — Temperature vs. resistivity curves for a
number of LaCrO₃-Cr systems [14]

1.	100% LaCrO₃	5.	50% LaCrO₃-50% Cr
2.	80% LaCrO₃-20% Cr	6.	40% LaCrO₃-60% Cr
3.	70% LaCrO₃-30% Cr	7.	30% LaCrO₃-70% Cr
4.	60% LaCrO₃-40% Cr	8.	20% LaCrO₃-80% Cr

The samples tested in Fig. 6 were 6x10x60 mm parallelepipeds prepared by compaction of fine powders of LaCrO₃ (<60μ) and Cr (<5-10μ) with subsequent sintering in argon at 1700°C. Figure 6 shows that metallic conductivity can be achieved with LaCrO₃ if the Cr content is at least 30 percent. The Soviets have shown preference for the 40 percent Cr combination for electrode testing in the U-02 and U-25. Figure 7 shows the undamaged appearance of LaCrO₃ (60 percent) - Cr (40 percent) cermet electrodes (anode) after 12 runs in the U-25 (the third vertical row from the left) [13,14].

According to open Soviet sources, the major breakthrough in lanthanum chromite development came about as a result of improved

Fig. 7 -- Electrode modules (anode) after 12 runs in the U-25
(LaCrO$_3$ is third module from left) [13]

fabrication techniques [62,63]. In 1974, the Soviet Institute of High
Temperatures reported the development in 1972 of a new method of synthe-
sizing lanthanum chromite of high purity and several technological pro-
cesses for preparing cermets from lanthanum chromite and chromium [13].
Soviet publications have described a new melting technique for preparing
LaCrO$_3$ that attempts to prevent high temperature reaction with, or
contamination by, the crucible material. U.S. materials specialists
do not believe the technique to be practical for large scale crystal
growth, but the Soviets have announced that they are trying to develop
it into an industrial process [63].

In conjunction with LaCrO$_3$-Cr cermet fabrication technology, two
interesting techniques were developed to improve the properties of the
final product: (1) introducing small quantities of palladium to in-
crease resistance to oxidation by one to two orders of magnitude, and
(2) using explosive compaction of LaCrO$_3$-Cr cermets to increase thermal
conductivity by a factor of two to three [14]. Figure 8 graphically
compares the oxidation resistance of a typical LaCrO$_3$-Cr cermet (curve 1)
in air at 1325°C and specially treated LaCrO$_3$-Cr cermets (curves 2-4)
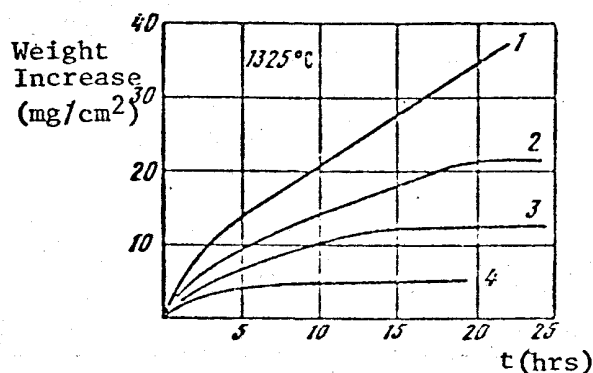[14]. Experience with lanthanum chromite cermets in the U-02 has been

Fig. 8 -- Oxidizability of LaCrO₃-Cr cermets [14]

Curve 1: Typical cermet in air at 1325°C
Curves 2-4: Specially treated cermets

sufficiently promising to continue their testing in the U-25, where more than one year's experience has already been gained [13].

IHT also developed a method for explosively compacting large ceramic samples using thick-walled tubes to prepare annular samples of LaCrO₃ cermets with diameters of about 100μ and thicknesses ranging from 20 to 30μ. Tests on such cermets showed that sharp increases in material density caused by explosion compaction, together with the resulting uniform structure of the cermets, served to reduce the material's oxidation rate in air at temperatures of 1500°C by a factor of two (in comparison with cermets prepared using standard powder-metallurgy techniques) [13].

The Soviets also had some early success doping LaCrO₃ with CaO,[*] first considered by A. V. Zyrin in 1967 [14]. The CaO dopant significantly improved the electrical conductivity of the compound. The tested samples were prepared by melting fairly large-particle (∿50μ) powders. The CaO was added in quantities ranging from 2 percent to 10 percent by weight, relative to equimolar mixtures of lanthanum oxide. The chromite was subsequently introduced in the form of a carbonate [14]. It was found that the CaO had a catalytic effect on the sintering process, and as long as the proportion of CaO did not exceed the limits of 5-10 percent

[*]The Japanese have patented CaO-doped LaCrO₃.

by weight, the open porosity values did not exceed 3-7 percent; 5-7 percent CaO content was found to be optimal from this point of view [14]. Figures 9a and 9b show the microscopic structure of two of the prepared samples [14]. Table 4 shows the experimental values found for the microhardness of the various combinations of $LaCrO_3$ and CaO [14]. The electrical conductivity tests with the above samples (Fig. 10) showed that conductivity
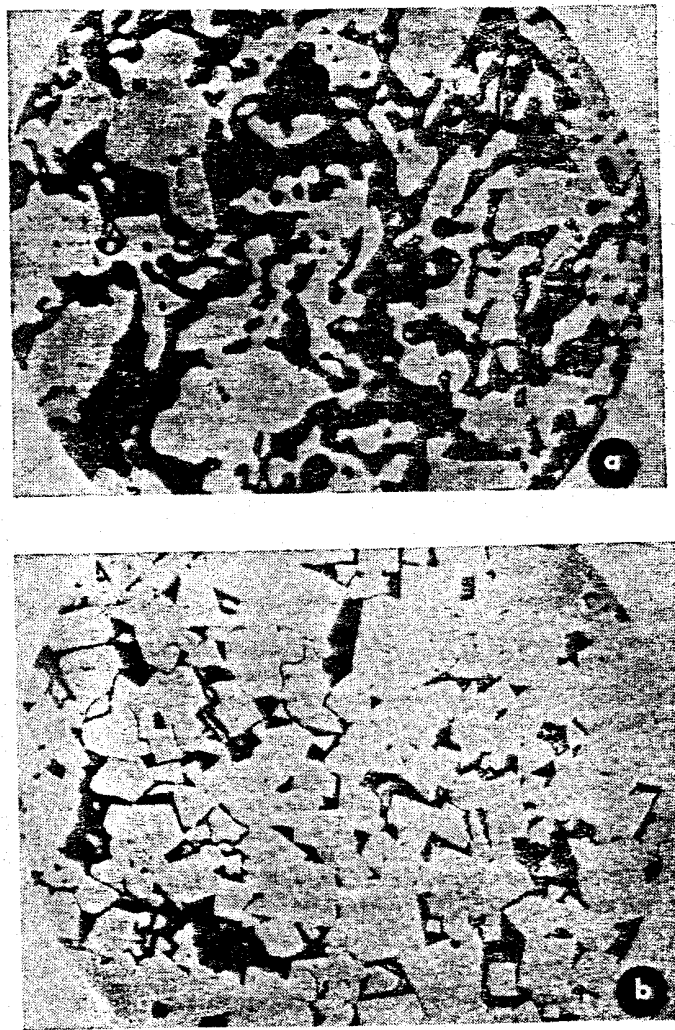

Fig. 9 -- Microphotos of samples of lanthanum chromite doped with CaO [14]

a: 2 percent CaO by weight
b: 7 percent CaO by weight

Table 4

MICROHARDNESS OF $LaCrO_3$-CaO [14]

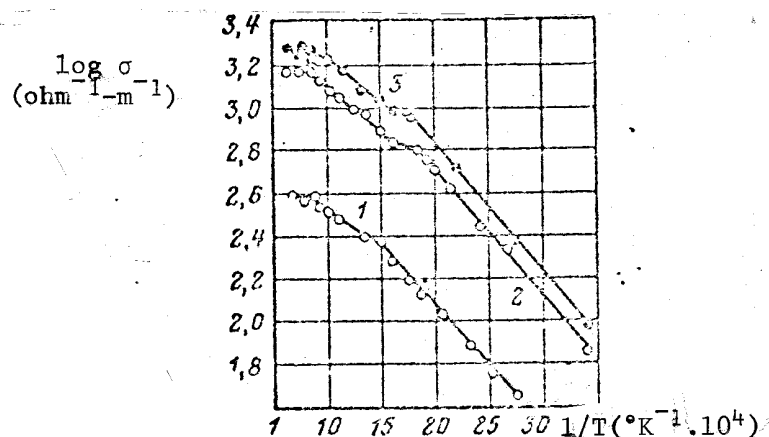| Quantity CaO (weight %)	2	5	7	10
Microhardness (kg/mm^2)	1013	1425	1145	1013

Fig. 10 -- Temperature vs. electrical conductivity plot
for $LaCrO_3$-CaO

1. 2 percent CaO
2. 7 percent CaO
3. 10 percent CaO

varied directly with CaO quantity, but the CaO did not suppress the poly-
morphic transformations in $LaCrO_3$ observed by H. S. Ruiz in 1967 [64].
The Soviets concluded that $LaCrO_3$ doped with at least 5 wt-percent CaO
would exhibit sufficient electrical conductivity to encourage its use
in MHD electrode applications [14].

The Soviet Academy of Sciences Institute of Physics (FIAN) has also
developed what they have termed *fianites*, crystals of refractory oxides,
which are stable and reportedly exhibit good electrical (conducting) and
thermal properties up to temperatures of 2500°-2600°C [62]. However, the
Soviets have traditionally been weak in terms of high-purity crystal growth

(especially large-scale growth of refractory oxide crystals) so that the latter work may not be as exciting as the Soviets report. As a matter of fact, the description of the above crystal fabrication technique is very similar to the refractory oxide work they reported earlier [65], which U.S. materials specialists reviewed and found to be rather ingenious but probably not capable of providing the rigid temperature control needed for large-scale crystal growth.

For a number of years the Institute of High Temperatures of the USSR Academy of Sciences has been conducting work on the development and investigation of properties of zirconia-based electrode materials. The properties of yttria-stabilized zirconia have been studied in the most detail. The Soviet comparison of data on the vaporization of refractory oxides [59], the results of mass-spectrometric investigations of the vaporization of zirconia solid solutions [56], and also information concerning the erosion resistance of these refractory materials [57] reportedly demonstrated that the application of yttrium oxide as a stabilizing dopant makes it possible to realize maximum temperatures at the walls of the channel, with preservation of the geometrical dimensions of the walls, the constancy of their face composition, and their electrophysical and thermophysical characteristics for a prolonged period of time [14].

According to Soviet data, the upper temperature limit of yttria stabilized zirconium dioxide for electrode applications in an industrial MHD generator is 1850°C at a mass flow velocity of 500m/sec. This estimate was made without consideration of the possible destructive effect of the emission process [15,22].

A number of rare-earth dopants have also been used by the Soviets to enhance zirconia-electrode properties. Figure 11 shows the results of Soviet resistivity tests of a number of ternary systems -- e.g., ZrO_2-La_2O_3-CeO_2 and ZrO_2-Nd_2O_3-CeO_2 [14].

In 1972, IHT developed ternary ceramic oxides using zirconia stabilized with oxides of rare-earth elements. These ceramic electrodes, extensively tested in the U-02, were shown to be capable of operating with power densities of up to 2 kw per electrode pair and current densities of up to 2 amps/cm^2. These results have been sufficiently encouraging for the Soviets to commit themselves to further development
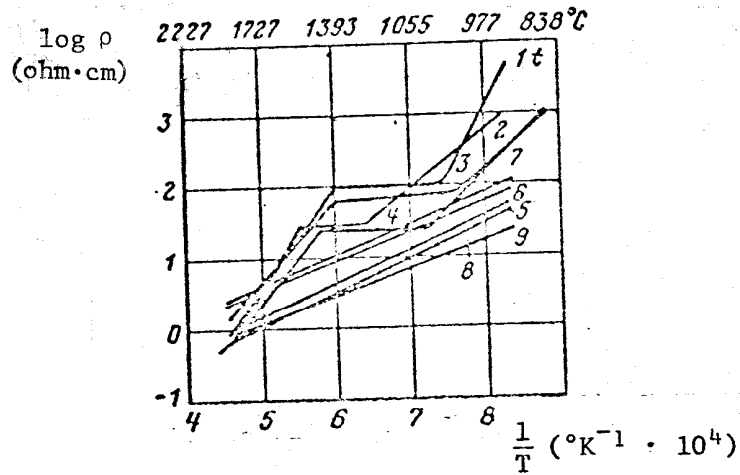
Fig. 11 -- Resistivity vs. temperature plot for a number of zirconia-
based ternary systems [14]

Curve No.	Composition Ratio (%)				
	ZrO_2	La_2O_3	CeO_2	Nd_2O_3	Y_2O_3
1	80	10	10	--	--
2	70	20	10	--	--
3	70	10	20	--	--
4	85	5	10	--	--
5	80	--	10	10	--
6	70	--	10	10	--
7	70	--	10	20	--
8	85	--	10	5	--
9	90	--	--	--	10

of ceramic-oxide electrodes for their U-25 installation. Current leadout
materials for this type of electrode were likewise studied, with the re-
sult that the CeO_2-Nb_2O_5 and CeO_2-Ta_2O_5 compounds and an alloy referred
to as No. 608 (Institute of Metallurgy) were found to satisfy the elec-
trical resistivity and oxidation resistance requirements [13].

Solid solutions of zirconia, praesodymia, and indium oxide were used in the fabrication of new ceramic electrodes with ceramic leadouts. A technology has been developed to fabricate electrode and leadout connections (nondetachable) so as almost to eliminate any potential difference between the two. Figure 12 schematically illustrates this type of contact configuration. The Soviets plan to use it in their hot channels [13].
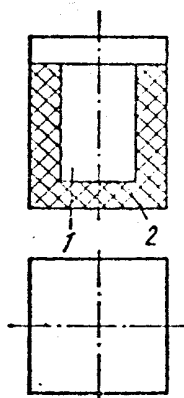

Fig. 12 -- Nondetachable electrode-leadout connection [13]

1. electrode
2. leadout

Laboratory tests were performed on these electrodes to determine their DC conductivity and structural strength under simulated MHD operating conditions. The test electrodes were exposed to current densities of 3-4 amps/ cm^2 (which is a considerably higher density than is necessary for commercial systems) for 269 hours in an air environment; the temperatures reached at the electrode extremes were 1350°C and 700°C. Results showed that the ceramic electrodes' resistivity decreased with increasing time of continuous electrical conductivity. Figure 13 is an I-V graph of the test results. Curves 1 and 2 were plotted at the beginning of the test run; curves 3 and 4, 10 hours afterward [13].

Additional testing showed that the same electrodes had a practical current density limit of 4 amps/cm^2 and a maximum operating temperature
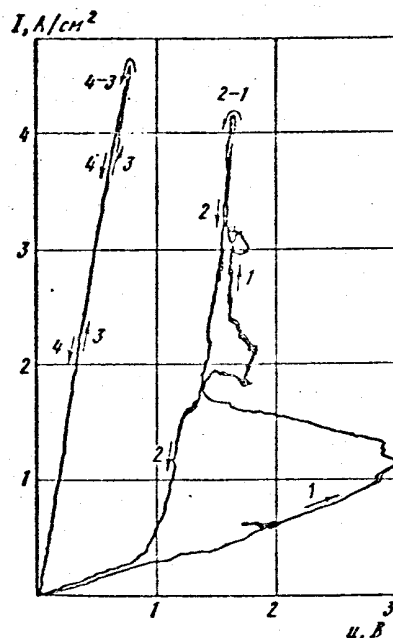
Fig. 13 -- I-V graph of test results for zirconia-praesodymia-
indium oxide electrodes with
ceramic leadouts [13]

of 2000°C. A 300-hour test run in a hot U-02 channel (50 hours of which
were in an oxygen environment) reportedly indicated these electrodes were
capable of long-duration operation with current densities of 2-3 amps/cm^2
and operating temperatures of 2000°C [13].

During 1972, IHT's chemical plasma facility (heated by a high fre-
quency generator) was reconstructed for the purpose of preparing zirconia
from zirconium tetrachloride in a high frequency oxygen plasma at tempera-
tures of 4000°K. The first samples of fine zirconia powder have already
been obtained and will be used to fabricate hot electrodes for testing
purposes [13].

IHT also has a continuing program (since 1970) for sintering powders
(microspheres) spheroidized in plasma. Very good results have been ob-
tained when these powders were compacted uniformly from all sides and
when activating agents were introduced into the intersphere contact
regions. Figure 14 shows a fractured material of spheroid powders
stabilized with zirconia. Because such material consists of individ-
ually treated (in a plasma) cross-connected structural microspheroids,

Fig. 14 -- Microphoto of zirconia stabilized spheroid-
powder material [13]

this type of structure reportedly does not undergo recrystallization at
temperatures below 2300°C [17].

IHT has also developed a technology for preparing spheroid powders
(in a plasma) with diameters of 50-200μ. In the case of ZrO_2/Y_2O_3, Soviet
petrographic studies have confirmed the formation (by plasma processing of
powders) of 100μ-diameter microspheroids with a polycrystalline structure.
Individual grains varied in size from 3 to 12μ. These materials are being
tested in the 1800°-2300°C temperature range [13].

The Soviets have studied silicon carbide extensively and still con-
sider it as having potential for electrode applications. They believe
its major advantage to be the possibility of decreasing the electrode
size as a consequence of the high electrical conductivity displayed at
a low temperature and a high thermal conductivity [14]. Considerable
testing of this material has also been done at the facility set up by
the Ukrainian SSR Academy of Sciences at their Institute of Electro-
dynamics in Kiev.

The Soviets have tried doping SiC with a number of materials, inclu-
ding chromium (which they claim considerably increases the maximum cur-
rent density tolerated by SiC electrodes), titanium (Fig. 15), and others.
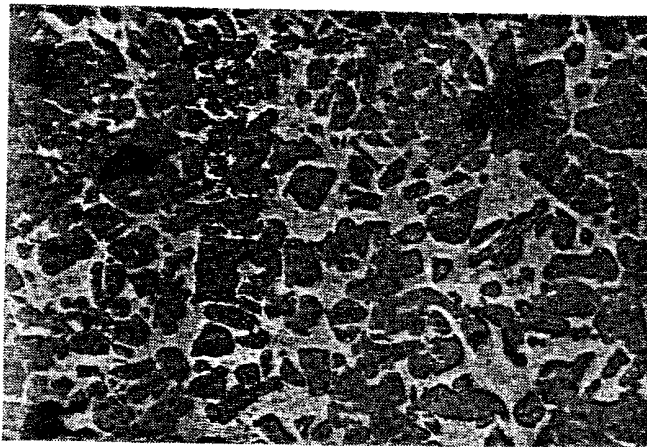Tests on titanium doped silicon carbide (in air in a temperature range

Fig. 15 -- Microstructure of a ceramic based on silicon carbide
and titanium [14]

of 20-1500°C) showed that structural strength increased with temperature, reached a maximum (because of the growth of binder plasticity), and then decreased [23].

The reaction of a ceramic based on silicon carbide with various gaseous media (air, water vapor, carbon-dioxide, nitrogen) was studied in a wide temperature range (1500° to 2450°C). The most hostile medium at all temperatures was water vapor, which, with respect to rate of oxidation, is three to four times as reactive as air [21,24].

The Soviets concluded [21] that increased material purity of doped SiC and structural improvements in cubic SiC binders would increase its strength and stability, making metal-doped SiC very attractive for low temperature operation (1400°-1700°C). At wall temperatures of 1700°-1850°C, ternary systems based on rare-earth-doped zirconia, which have considerably greater electron conductivity at MHD operating conditions than binary zirconia systems, can be used. They also found that lanthanum chromite could be very useful in current leadouts for hot electrodes, because of its high electron conductivity and reduced cost (compared with present current leads of costly noble metals) [14].

COMPOSITE MATERIALS

It is important to distinguish two kinds of composite structures: first, the typical composite structure in which there are two or more phases in a rather uniform distribution throughout the thickness or the length of the sample, and which may even be of the fiber reinforced variety; second, the type of composite structure in which one starts with a sheet of one material and goes through either integrated steps or through a gradation to an end material. U.S. scientists showed the Soviets a sample of the second type of composite structure that might be used for an electrode. One face is of silicon-carbide titanium-diboride ceramic of theoretical density; the back face is titanium metal. The cross-section thus changes composition in graded steps so that one goes from a ceramic to a metallic matrix. In discussion with U.S. specialists, the Soviets expressed great interest in this type of composite structure.

So far, the Soviet MHD composite materials program has apparently focused on investigating magnesia-matrix ceramics reinforced with single-crystal magnesia fibers (as insulators); initial results show greatly improved high-temperature durability [13]. Figure 16 shows the structure of a sample of the material currently under study. The United States has not yet considered initiating a coordinated effort in this area.

The use of composite fiber structures in MHD technology has been suggested in the United States, but no research has been undertaken. The Oak Ridge National Laboratory attempted to develop a high strength UO_2 composite by incorporating tungsten or molybdenum wires in a UO_2 matrix. The material was thought at one point to be applicable to thermionic power generators. This type of structure was also thought to be appropriate for MHD applications. The chief problem with these and similar systems is the reactivity of the fiber reinforcing materials. The Soviets are believed to have considered this as well, but they appear more interested in the other graded type of structure in which perhaps a two-phase or three-phase material goes from one highly stable material to a more conductive, machinable, and plastic material. The key to formulating composites, of course, is matching the thermophysical
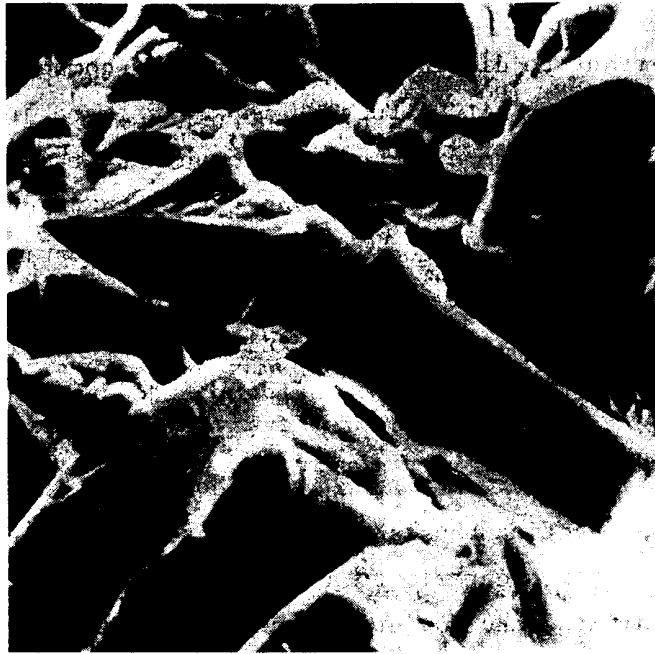
Fig. 16 -- Microphotograph (3000X) of a single-crystal-MgO-fiber
reinforced MgO composite ceramic [13]

properties, which must be very similar not only at the fabrication
temperatures down to room temperature, but also from room temperature to
the use temperature. Chemical compatibility at the operating temperatures
is also important. Some U.S. materials specialists believe the chromium-
lanthanum-chromite cermet has more importance and redeeming value in
that it tends to stabilize the chromium oxide. For example, the Soviets
use it primarily to back the zirconia-based electrodes (although they
have also tested it as an electrode with some limited success). Since
there is always some oxygen migration, the chromium metal is available
as a receiver of the oxygen and can maintain the chemical and electrical
stability of the current leadout. If what the Soviets have been saying
is true (and their recent publications support this view [66,67]), their
primary electrode materials at this point are the zirconia-based compounds.
The silicon-carbides and lanthanum-chromites may be available for low
temperature applications or in the area of current leadouts, but only
the zirconia-based compounds are apparently currently being considered
for their high-temperature electrode/plasma interface.

V. ANALYSIS OF CANDIDATE MATERIALS

The most successful material in MHD electrode applications (both
in the United States and Soviet Union) has been stabilized zirconia.
However, a number of shortcomings inherent in zirconia make it undesir-
able to some U.S. materials specialists. First, the conductivity of the
zirconia-based materials is too low; and second, it is not an electronic
conductor totally, and therefore will always have problems related to
electrochemical oxidation at the anode backing interface. Furthermore,
the same specialists say it is not a stable electrode material at high
voltages (current densities). The British have reported many experi-
ments in which the voltage builds up because of ion blockage until the
material decomposes by electrolysis. The Soviets also apparently be-
lieve this. They have reported experiments showing that such voltages
are very small (a few volts per centimeter). The zirconium dioxide
decomposes to form free zirconium metal and Zr_2O_3, which is essentially
a runaway process because the zirconium metal at grain boundaries then
provides a high conducting path causing localized heating and eventual
blackening or channeling of the material. And, in fact, the blackened
zirconium dioxide is degraded to such a state that it easily crumbles.
U.S. materials specialists stress that an ionic conducting electrode,
even if it is only partially ionic (.01 for the transference number),
represents an unstable electrode configuration. Because of the thermal
gradient across the electrode, the absolute resistivity and its tempera-
ture dependence must be small -- i.e., the integrated resistivity, the
resistance must be small [68]. Zirconia is poor in this regard.

It is now the conclusion of the Soviets as well as the Americans
that only high temperature electrodes should be used in commercial MHD
generators, although the Soviets had indicated previously that they did
not experience intolerable losses with their cold copper electrodes. They
have apparently changed their point of view, and, in fact, at the recent
Moscow Symposium Sheindlin indicated that Soviet studies showed that higher

efficiency could be gained by using hot electrodes, but the main reason for going with hot electrodes is to avoid the most damaging effect -- that caused by arcing through the cold boundary layer. Therefore, both the Americans and the Soviets wish to get the electrode interface as hot as possible. This leaves one in a predicament, for at very high temperatures the boundary layer problems will indeed be reduced, but the potential for vaporization and certainly preferential vaporization of doped compounds will be marked. One merely has to go through the Periodic Table to see which elements or compounds are stable with respect to vaporization, oxidation, sulfidation, and temperatures on the order of 2000°C. And one easily recognizes why the MHD channel-builders were fascinated with the potential of zirconium dioxide; it has a high melting point and low vaporization rate. Uranium dioxide is the only simple oxide currently known that has an equivalent melting point but better electronic properties and for which there is a great deal of mechanical and thermodynamic data.

One could conceive of using depleted UO_2 to construct electrodes, but only if the base radioactivity of this material can be shown to be low enough that it does not constitute an environmental health hazard. It is very resistant to sulfidation, to decomposition through oxidation, and to vaporization losses. There are technologies for sintering it to full theoretical density; coating it; plasma spraying it; vapor depositing it; and making it in thick films, thin films, and single crystal form. Its compatibility with other oxides, insulators, and metals is well documented in the AEC literature. So if one had to build an MHD system today operating on clean fuels (with no condensed layer), such as would be the case for military applications, uranium dioxide should probably be considered as a promising candidate material.

Another candidate material, thorium dioxide, has the problem of radioactivity. As yet no one has found a dopant to make it an electronic conductor, so there is no reason to consider it except possibly in special applications where an insulator would be required and the problems of toxicity or radioactivity could be tolerated.

In commercial MHD systems, the zirconia-based compounds are of interest primarily to the Soviets and to Avco and Westinghouse. In the proposed Westinghouse scheme, temperatures would be maintained above the condensation range of the slag constituents (>1800°C). This would avoid electrode degradation by molten slag. Thus, Westinghouse would need an electrode that operates at extremely high temperatures but functions with a dirty hydrocarbon; yet the electrodes would operate, like the Soviet electrodes, in a "clean" mode. U.S. specialists who consider that slag may be used to advantage in MHD materials development are skeptical about this approach; and, as they further point out, zirconia stabilization at high temperatures remains a major problem. Figure 17 schematically illustrates the reactions occurring at a zirconia-based anode.

Zirconium dioxide undergoes a phase change at about 1100°C with a subsequent volume change; therefore one must stabilize the crystal structure. Generally, this is done by doping with magnesia or calcia. However, yttria and ceria can also do the job. In stabilizing with calcia, magnesia, or yttria, the ionic conduction is increased to high values. The conduction is through the vacant oxygen lattice sites, which are increased in number because of the different valence of the cations of the dopant. In fact, the ionic conducting zirconias have potential use in fuel cells and batteries because the charge transport is specifically due to ions. This zirconia was first tried in the short duration tests in almost all MHD facilities, and it appears to be particularly unstable when there are blocking electrodes. The U.S., as part of the joint U.S./USSR program, however, has proposed to test one channel module in the U-02 facility based on the zirconia-calcia or the zirconia-yttria system as a benchmark.

The Soviets and French, as well as the Americans, have examined zirconia-based compounds doped with rare earths for creating electronically conducting zirconia. Ceria seems to be the least expensive and most effective dopant in this regard. The Soviet and American work indicate that the ternary system of zirconia-yttria-ceria is very stable from a thermochemical point of view. However, very slight additions of yttrium to a zirconia-ceria electrode increase the ionic nature of the
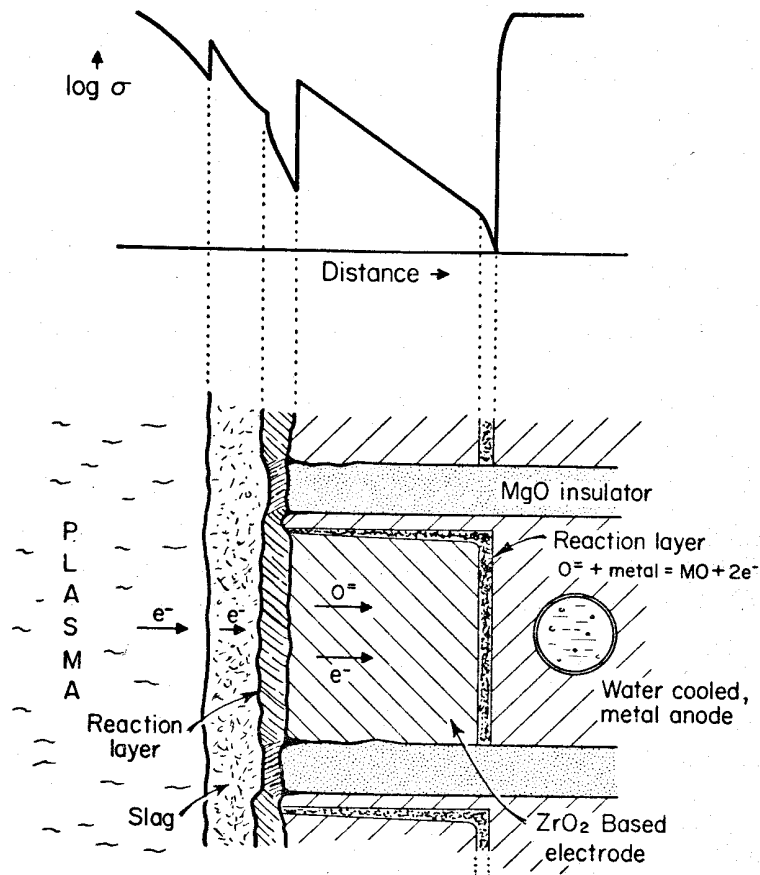
Fig. 17 -- Schematic reactions occurring at a ZrO_2-based anode [2]

conductivity. U.S. visitors to the Soviet Union were shown calculations indicating that Soviet data were similar to those of Fehrenbacher here in the United States [69], so there do not seem to be any large discrepancies in measured transference numbers.

Other dopants have been added to zirconia, but they all had the net effect of increasing the electronic portion of the conductivity. For example, praesodymium, titanium, and neodymium have been tried. The Soviets report that neodymium is about as effective as cerium [14,15], which is rather confusing. The neodymium should tend to form a +3 ion and be stable, but it is the multiple valency state of the cerium ions that enhances the electronic conductivity.

Several schemes for extending electrode longevity have been patented, including a series by Avco in which metal screen current leadouts (to minimize electrolysis) and zirconia electrode replenishment have been proposed. The one that appears to have considerable merit is the replenishment through the gas phase rather than replenishment of solid material from the back of the electrode that moves slowly to the electrode plasma interface. The original tests were made in about 1962 by Louis and Blackburn at Avco. Subsequently, the program was taken over by Brogan, and he reports to have replenished zirconia electrodes by adding zircon sand. Zircon is a zirconium dioxide/silicon dioxide compound, which disintegrates at high temperatures. The decomposition products then condense out on the generator wall as zirconia. The precise mechanism for this process has not been defined, but it is conceivable that the liquid silica from the zircon decomposition reaction aids zirconia adherence to the walls.

A few years ago, when Avco received monies to build a long-duration generator test facility, they decided to test these concepts of electrode replenishment for operation of the channel over long periods of time. This was to be a technology feasibility study. The results were mixed. They added zirconium dioxide grain to the combustor and found that they were in effect sandblasting the channel walls (because zirconia melts only at about 2800° centigrade). Thereafter, they reasoned that since magnesia and zirconia form a eutectic at a much lower temperature they could resolve the problem by adding magnesia granules and zirconia granules. This system, however, also sandblasted the electrode walls; apparently insufficient residence time is available for the particles to collide, interact, and melt as a eutectic liquid adhering to the walls.

Zirconia is perhaps the most difficult material to replenish because the free energy of formation of zirconium dioxide is of such a large negative value that there are very few volatile zirconium compounds, and it is therefore difficult to obtain a high vapor pressure with the zirconium compounds in the plasma to supersaturate it and cause deposition on the walls. Furthermore, there appears to be a significant difference between trying to deposit electrode material and merely supersaturating the plasma

or a slag layer to retard the degradation of the electrode. An alternative approach utilizes a special low velocity plasma for replenishing, during which time no MHD power is generated.

Some MHD channel designers have attempted to use zirconia cements and to trowel these in at the start of the run. This may be appropriate for very short duration experiments but it appears to be in the wrong direction for providing thermomechanical stability to the electrode material. First of all, all ceramic cements contain low melting phases, such as phosphates and silicates, which glue the body together and therefore lose mechanical integrity at high temperatures. Another deficiency of these cements is that the bonding phases generally do not conduct the electrons as well as required for MHD electrodes.

Very dense zirconia bodies can be prepared, but this requires special processing. Commercial zirconia, which is of lower density, contains several percent of silicon dioxide, which degrades mechanical properties at high temperatures. Another commonly understated materials problem in the United States is thermal shock. The pulsing of the plasma can produce thermal fatigue stresses (similar to those encountered in turbines) and zirconia is generally not very resistant to this type of thermal shock.

Metals, graphite, or the diborides and carbides have properties many times better than the oxides. It has been well established, however, that zirconia can be prepared with two phases present, the cubic and the monoclinic phases, and that they produce ultrafine microcracks giving the material stability against crack propagation. These schemes are not known to have been applied to the use of the zirconia compounds as electrodes.

The next oxide proposed by most MHD designers is lanthanum chromite. Since it does not have a sufficiently high electrical conductivity, it is typically doped with a calcium oxide or a strontium oxide. It was initially thought that these dopants improved chemical stability. However, some now believe that perhaps they simply improve sinterability and conductivity but not stability -- i.e., the doped chromite still vaporizes as CrO_2 or CrO_3.

Presumably, if one adds a dopant that stabilizes the chromium oxide one can retard the vaporization. It has been recently shown that one can sinter chromia and chrome-magnesia refractories by carefully controlling

the oxygen pressure above the bricks. This was a critical problem because the chrome magnesia bricks are important in steel-making. One could never sinter at high enough temperatures to get high densities, because chromium oxides tended to volatilize. Moreover, the preferential volatilization reduced the surface driving forces for sintering. However, when a partial pressure of oxygen at the equilibrium level of the metal-chromium oxide phase boundary is maintained, preferential vaporization is retarded and very high temperatures can be used to obtain the high densities required for refractories [70,71].

In this country, the ability to fabricate lanthanum chromite has not yet been proven on a commercial basis. General Refractories in Philadelphia claims to have powders and sintered material available. However, some scientists who have purchased this material have found that it fell apart when sitting around the laboratory, probably because of the hydration of excess lanthanum oxide. The Franklin Institute in Philadelphia carried out a proprietary research program for General Refractories outlining the precise procedures for fabrication, and it is probable that good lanthanum chromite can be made.

The University of Utah, as part of their NSF grant project, is also studying the fabrication of lanthanum chromite and is believed now to have good material [43]. The Japanese have also fabricated lanthanum chromite (with calcium doping). The Asahi Glass Company has a patent [72] on this material and is fabricating it for furnace heating elements (and in fact claimed to have operated them at 2000°C for many hundreds of hours). The sample viewed by U.S. researchers was dense and did not crack after having been left in moist air over a period of many months. There is, however, some hysteresis in the high temperature electrical conductivity. The Norton Company reports that they also regularly fabricate lanthanum chromite and have it available, but few specifics are known about their compound. It would appear that lanthanum chromite is not as difficult to fabricate as the Soviets claim. In the United States, it would merely take someone to indicate interest in the material and there would probably be several companies available to fabricate it.

The Americans, French, and British have considered lanthanum chromite as the principal electrode element because it has a much better electronic conductivity than the zirconia-based compounds and because the conductivity has a very low temperature dependence. The recent flourish of activity in the Soviet Union made visible by the U.S./USSR cooperative program indicates growing interest in lanthanum chromite as a current leadout element rather than as the primary electrode element (at least that is what U.S. materials specialists saw in the U-25 facility, and that is what they have been told on several occasions). Their literature suggests primary interest in zirconia-based materials for the electrode application. The Soviet lanthanum chromite-chromium cermet is reportedly favored for the leadout application.

The purpose of the chromium metal phase in the cermet, besides improving mechanical and thermal properties, is to lower the oxygen activity, retarding the oxidation/vaporization of chromium much in the way that is accomplished in the sintering of chromium magnesia refractories. The chromium metal will become oxidized when the composite zirconia-based electrode and cermet are exposed to high temperature generator operating conditions. The extent and rate of oxidation at the anode interface is difficult to predict. The Soviets claim to have observed no such complications, but U.S. specialists see no way to avoid the problem -- i.e., the oxygen will move to the interface and react with the chromium constituent of the lanthanum chromite-chromium cermet. A rough estimate of oxygen ions at the current leadout, when partially ionic-conducting zirconia is used, provides persuasive evidence that the problem must be there:

$$\text{moles pf } 0^= \text{ ions} = \frac{\text{(current density) (transference number)}}{\text{(Faraday const.)} \times \text{(equiv/ion)}}$$

$$= \frac{(1 \text{ amp/cm}^2) \ (0.1)}{(96,500 \text{ joules/volt} \cdot \text{equiv}) \ (2 \text{ equiv/ion})}$$

$$\approx 5 \times 10^{-6} \text{ moles } 0^=/\text{cm}^2 \text{ sec}$$

$$\approx 2 \times 10^{-3} \text{ moles/hr cm}^2$$

Assuming that the $O^=$ oxidizes Cr to form Cr_2O_3 and that all the oxygen at the anode forms a resistive chrome-oxide layer, the rate of the resistive layer growth (r) can be expressed in the following terms:

$$r \approx (2 \times 10^{-3}) \ \frac{(density)}{(molecular \ wt)} \approx 0.02 \ cm/hr.$$

On this basis, if the $LaCrO_3$-Cr cermet contains 20 percent Cr metal (the Soviets have used Cr concentrations of 20 percent to 80 percent in their experiments [11]), the resistive layer growth rate goes up to about 0.1 cm/hr. The problem may not become apparent in short duration experiments, but with longer operating times, the progressive oxidation of the metal phase in the cermet could be expected to affect performance significantly.

The Soviets reportedly do not see any possibility of using lanthanum chromite above about 1500° or 1600°C, which further reinforces the view that their interest in the material must be in terms of an electrode back-up rather than as a high temperature surface. This points out the potential advantage of a slag coating. If it is saturated (such that the corrosion is minimized) the surface of the lanthanum chromite could be maintained below 1500° or 1600°C while the surface of the slag-coating/plasma interface could be maintained at 1700° to 1800° centigrade. The boundary layer thickness in the plasma then would be much smaller and the arcing problem would be greatly reduced. A very tenacious slag coating (typically very viscous liquid oxides) should provide a self-healing capability in the event of local spallation or volatilization of the surface layer by the thermal transients or arcing effects. Proof of these concepts are scheduled to be carried out in 1975 in a small test at MIT.

The carbides, borides, and nitrides are the next important class of compounds. These show generally good mechanical properties and, if transition metal cations or dopants are used, good electrical conductivity as well, several orders of magnitude better than even lanthanum chromite (see Fig. 2). In addition, thermal expansion coefficients are usually low and thermal conductivity is high, both of which favor improved thermal shock resistance. (For this reason, and

because of their high strength, silicon nitride and silicon carbide are being developed for high-temperature gas-turbine service.)

The same problem that limits the non-oxide ceramics for MHD electrode application exists for high temperature metals; the protective oxide coating that forms on these materials in service tends to volatilize or spall under MHD operating conditions. For silicon carbide or the zirconium diboride/silicon-carbide system, the oxide is primarily SiO_2. As this layer grows, electrical resistance increases. At about 1500° centigrade, however, the vaporization losses are such that the material itself begins to be lost at a rate intolerable for MHD applications [67].

In general, when a protective scale forms on stainless steel, aluminum, or silicon carbide, the same oxide properties determine both the degree of protection and the insulative quality of the scale. To avoid thick scales, oxygen diffusion through the scale must be slowed (conversely, the metallic cation must be prevented from moving rapidly to the scale-gas interface). The other possible rate-limiting step is the migration of either electron holes or electrons that move slowly in insulators. Thus, nickel oxide, cobalt oxide, chromium oxides, and aluminum oxide that form on high temperature alloys do not conduct electrons readily, nor do they conduct ions very rapidly. This is necessary for the formation of a stable oxide scale.

Because of the inherent problem in high temperature applications, these materials have been considered by all MHD channel designers but have been discarded in the end because they cannot operate above approximately 1500°C. There has been a scheme proposed, however, where the silicate slag coating is made to protect the diborides and the carbides in such a way as to allow their potential use. Again, the surface of the slag layer to be operated would have to be very hot to minimize arcing.

As was pointed out at the Soviet symposium and at the Tullahoma Conference, it is critical to understand the protective mechanism -- i.e., the saturation of this layer so that excessive degradation does not occur. If the iron content of the slag is as has been indicated by most assays on U.S. coal, there should be enough self-doping to

allow the reaction layer to remain sufficiently thin, conductive, and hot as to operate well. The rate of degradation is critical to the eventual use of any of these materials, but some U.S. specialists believe there are a number of other physical properties that are even more important. These specialists believe that the latter point cannot be emphasized enough, because the Soviets are apparently encountering thermal shock and other problems and also because American designers are perhaps not giving sufficient credence to the fact that the thermal expansion of insulators, electrodes, and metals must be matched and that the thermal stress induced by heating and cooling (start-up and shut-down) often is the eventual cause of serious failures.

The Soviet MHD committee seems to be very concerned about the thermal-shock and thermal stress problem, and perhaps this is the reason that they have attempted to develop the single-crystal ZrO_2-fiber-reinforced zirconia and the single crystal MgO-fiber-reinforced ceramics described earlier (the latter material for insulator applications). They have not talked about using these materials in any of their operating systems, and it is presumed that such materials would be quite expensive. The emphasis in the U.S. effort in composites appears to be away from adding boron or sapphire fibers to a metal matrix and more toward controlled solidification of ceramic materials, but many U.S. materials specialists do not believe that there will be widespread application of these materials in the near future.

If slag can be used to minimize the oxidation or vaporization of carbon (CO or CO_2), graphite becomes a viable electrode material. Graphite has about the best properties one could think of for an MHD electrode, except for its very high oxidation. It is extremely easy to machine, it is extremely thermal shock-resistant, it has very good conductivity, and it is stable at 4000°C.

By a similar argument, one can speak of tungsten or molybdenum electrodes. Molybdenum and tungsten also form volatile oxides. For example, molybdenum trioxide vaporizes so rapidly that if one places a piece of molybdenum metal in a furnace at 1500°C all one can see is a dark cloud form as the molybdenum oxidizes.

The basic principle revolves around a kind of kinetic equilibrium [73] in which the rate of migration of oxygen through the slag layer coating to the interface determines the material's lifetime. Initial studies suggest that this principle may well work, particularly with graphite. With graphite it might be easier to coat the electrode surfaces with a thin layer of silicon carbide so that it would oxidize to SiO_2 during start-up and considerably reduce graphite losses at the beginning. If a generator were to lose one or two centimeters of graphite electrodes coated with slag over 10,000 hours of operation (as may be the eventual case), the cost would be minimal. Graphite likewise should probably be a contender for electrodes in short duration military applications of MHD. The technology to coat graphite with silicon carbide is available, so there should be no problems in obtaining the needed material for short duration operation, but a number of generator designers do not believe graphite can be made feasible in a commercial system.

The concept of slag coating is distinctly different from what has been proposed in the past and opens the way to consideration of a wider spectrum of compounds that could not be seriously considered for non-slagging conditions. Some U.S. materials specialists strongly believe that a baseload facility could be developed on this principle.

It may very well be that the solution to the electrode problem in a coal-fired system rests in the protective nature of the slag coating. It is in the clean-fired system, such as the Soviet system or the Westinghouse scheme, where some U.S. specialists do not believe that there is currently a viable high-temperature electrode material.

For a short duration (ten-minute run time) generator, the thermo-mechanical problems should outweigh some of the other considerations. The material with the best thermomechanical properties would probably be silicon carbide, perhaps similar to the scheme shown in Fig. 18 in which silicon carbide is connected to a crude iron or copper base and the insulator is silicon nitride. These materials would be compatible and of very high strength; and, in a ten-minute run in which the service temperature was around 1500°, 1600°, or even 1700°C, one should not

TiB₂ (+SiC)

graded
structure

Ti-metal

Cooled
Fe or Cu

Insulator

MoSi₂

Mo

Cooled
Fe or Cu

Insulator

SiC

Graphite

Cooled
Fe or Cu

Insulator

SiC
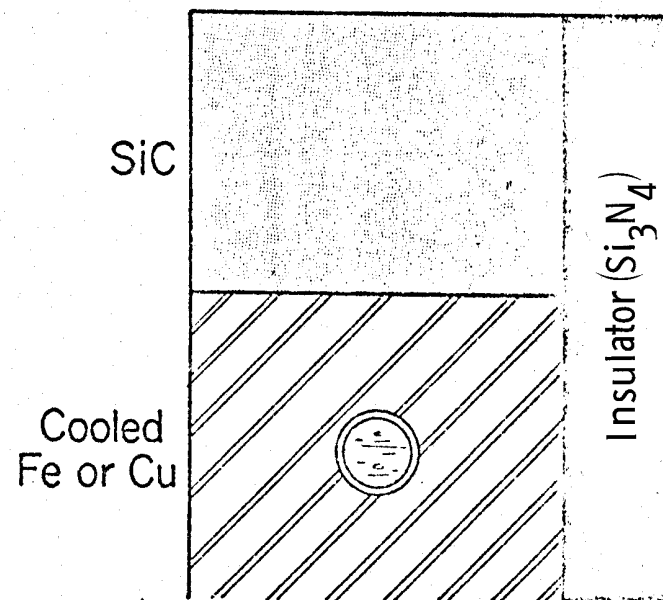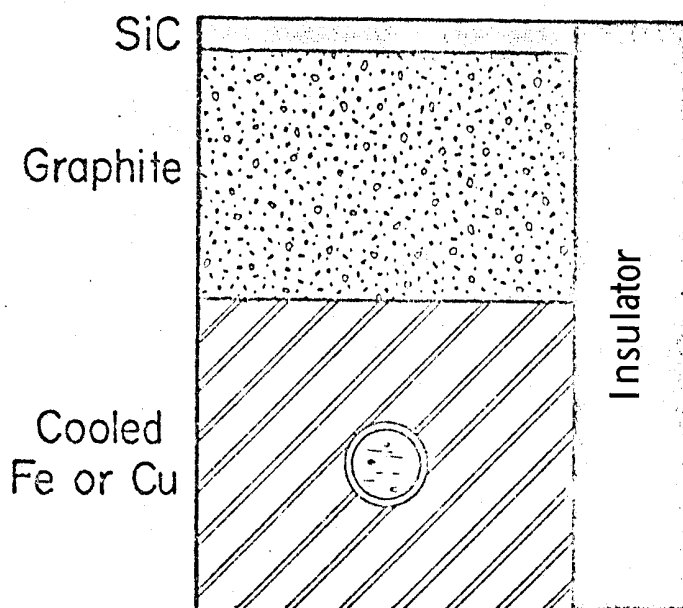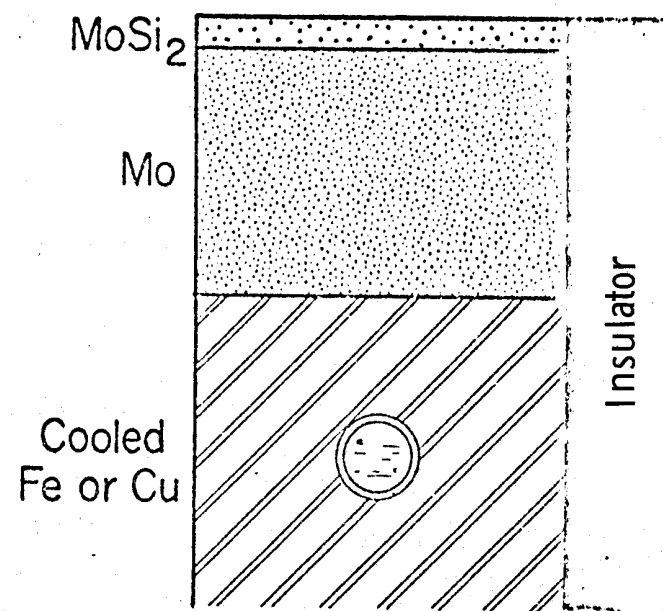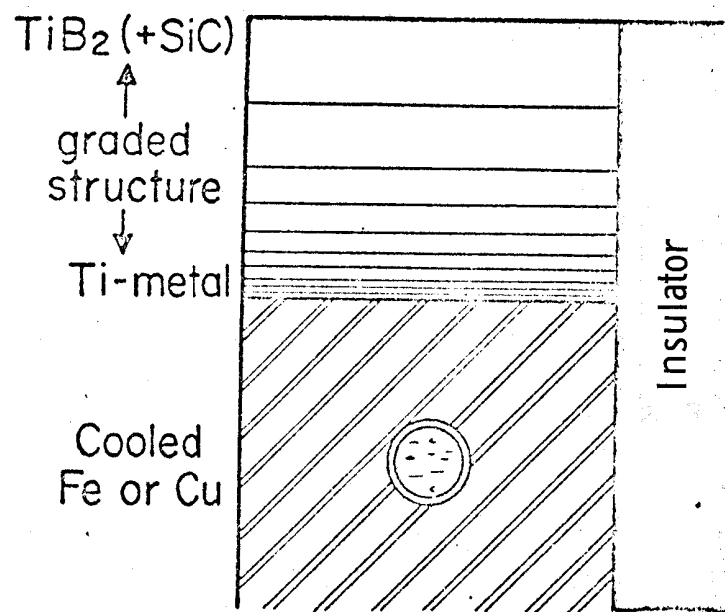
Cooled
Fe or Cu

Insulator (Si₃N₄)

Fig. 18 -- Possible electrode module configurations [2]

53

have too great a loss. The question is how many of these ten-minute runs are required for some mission before repair could be tolerated. The ARPA-funded gas turbine program, as well as corporate interest at Westhinghouse, General Electric, and United Aircraft, and others, has resulted in the development of extremely good silicon carbide and silicon nitride. This accumulated experience is supplemented by similar interests of such ceramic companies as Carborundum and the Norton Company, which is generally credited with doing the leading commercial work with respect to silicon carbide and silicon nitride.

The integrated electrode/insulator/current-leadout module has received very little attention in any of the past U.S. programs. There are indications, however, that this aspect will receive greater stress in the future programs. MIT, for example, recently proposed [5] a very interesting potential module compatible with coal slag and high current densities. It is a graded $FeAl_2O_4$-Fe_3O_4 structure with low resistivity (Fig. 3), a dense Al_2O_3 insulator, and an iron current-leadout.

Some U.S. materials specialists have taken the view that once the electrode problem is resolved, the insulator will prove to be the next major problem for long duration facilities. At very high operating temperatures (in a dirty environment) with the possibility of inter-diffusion and reaction between the electrodes and insulators, the insulator will tend to be conducting at the high temperature [74]. Although it will not act as an electrode directly, it should never-theless give sufficient leakage to cause problems in generator perfor-mance. All materials become conductors at very high temperatures, so that in the very high temperature regime envisioned for the Russian or the Westinghouse schemes, this should definitely become a problem.

Our present technology in the United States allows us to fabricate high purity, high density insulating ceramics. Those based on aluminum oxide or magnesium oxide are readily available. It appears that the Soviets and the Americans are having problems on taking dense electrodes and dense insulators and putting them together in an integrated package. There is evidence indicating that both countries use a cement inter-mediate, which some believe may in itself eventually cause problems in long duration facilities.

Investigations are currently being conducted on various oxide electrical insulators for the channel of an MHD generator at the Soviet Institute of High Temperatures and a number of other organizations such as VostIo (Eastern Institute of Refractory Materials of the USSR Academy of Sciences), UNIIO (Ukrainian Scientific Research Institute of Refractories), KhPI (Khar'kov Polytechnic Institute imeni V. I. Lenin), MKhTI (Moscow Order of Lenin Chemical Engineering Institute imeni D. I. Mendeleyev). This research is being conducted in the following three directions [13,33]:

1. investigation of ceramic materials based on the oxides of magnesium and aluminum, and also magnesium spinels and zirconates;

2. development of high-melting concretes based on magnesia and alumina fillers and various binders (high-alumina cement, aluminophosphate, barium-alumina cement, magnesia binders, and others);

3. search for thin-layer oxide coatings applied by gas flame or plasma spraying (mainly onto an alumina base).

There are also further considerations with the design of the module, particularly with respect to the way one extracts the current induced by the Hall field. According to some U.S. specialists, one probably should have a thicker electrode at the downstream edge than at the upstream edge so that the cross-section of the electrode (rather than being rectangular as it typically is) would be more trapezoidal. This would increase the resistance at the edge where the arcing is predominant. Thus, the design can be an important auxiliary tool in reducing the degradation mechanisms.

It has also been suggested [75] that a less conductive slag coating would be effective in spreading out the current and reducing arcing. Some very novel design approaches have been considered using a metallic and insulator base in which the real electrode would be just the condensed slag itself. By varying the amount of cooling, the resistivity/conductivity of the

slag can be varied along the duct. Again the design of the cups and the configuration could lead to improvements in the generator performance.

In the UTSI facility, where cooled copper electrodes are used, if one calculates the I^2R heating for the current densities that they have extracted, it is easy to believe that there is enough local heating to keep condensed slag layers in a liquid state. The available information suggests that below about 1300°-1350° centigrade the slag changes from a multiphase liquid to a solid. However, the conductivity drops off appreciably, so that a solid slag (even one containing iron) against a cooled copper electrode will be sufficiently resistive that the I^2R heating will keep it molten. Avco is also now testing slag-coated metal electrodes.

VI. CONCLUDING REMARKS

Judging by the quantity and content of the Soviet open literature, the Soviet Union has had a large, continually expanding and broad-spectrum program on MHD materials development for a number of years (probably since the early 1960s). In the early 1960s, the Soviets began to develop a small-scale model of a complete commercial MHD plant, the U-02, which has served primarily as a testbed for new MHD materials since its completion in 1965. Such a testbed facility (along with the much larger U-25, which has similar capabilities) is unique and provides the Soviets with an excellent capability for testing and evaluating promising candidate materials in a realistic commercial-MHD environment. The U.S./USSR cooperative program on MHD will give U.S. researchers access to both of these facilities for materials testing and operating U.S. built channels.

On the basis of open U.S. and Soviet literature, the main progress in MHD materials development over the years has been not so much in developing new materials as in improving electrode and insulating wall design, gathering additional data on known materials, and formulating new concepts for resolving materials deficiencies -- e.g., electrode replenishment and coating. Recently reported Soviet work with lanthanum chromite (doped with chromium) and the recently initiated Soviet composite material development program, however, may represent a step in the direction of new materials development.

The United States, by contrast, has comparatively neglected MHD materials development, apparently because of the funding constraints imposed by the overall U.S. MHD program and because the early U.S. program emphasized military generators, where the short time factor made materials problems much less severe. New materials development has not been stressed in the U.S. MHD program until the present fiscal year. However, both U.S. and Soviet materials technology has already reached a stage where a short duration generator can probably be successfully constructed.

For example, available estimates [76] of the recession rates for plain molybdenum and graphite MHD electrodes (approximately 1×10^{-4} cm/sec when the electrode surface temperature is above 700°C) suggest that they would survive short duration operation, even under high velocity MHD conditions that would increase the material loss rate. The rates are dependent on diffusion of the gaseous reaction products from the surface and thus are sensitive to boundary layer thickness. In each case the material recession rate can be greatly reduced by a protective silica film -- e.g., SiC-coated graphite and $MoSi_2$ coated molybdenum. On this basis, some U.S. specialists have estimated that such a 5mm-thick electrode coating would last about 60-100 minutes in an MHD generator fired in a short-burst mode with "clean" fuel. Performance would be penalized, however, by formation of a SiO_2 scale on the electrode surface.

The feasibility of a commercial MHD generator is highly dependent on the development of a material capable of surviving sustained long-duration operation in a coal-fired MHD environment. Neither country has yet found such a material.

Neither country's MHD materials research program has yet progressed to a sufficiently advanced stage to assess the relative state of the art very precisely. And, while the U.S. program has underemphasized materials development and the USSR has stressed it, the two countries appear to be at about the same level. The Soviets have, with limited success, studied many more materials and under more realistic conditions than has the United States, while the United States has developed electrode coating replenishment techniques to extend the useful lifetimes of already known MHD materials.

The two national programs are now undergoing some change. In the last two years the USSR (at the Institute of High Temperatures and the Institute of Physics) has shown increased interest in fiber-reinforced composite materials and refractory oxides, but the Soviets are encountering difficulties in obtaining the sufficiently pure refractory oxide crystals needed for the MHD application. The U.S. program for the first time this year has adequate funds available to initiate an integrated MHD materials development effort.

If U.S. funding levels for MHD research continue to increase, the
United States could forge into the lead in the materials development
area. At the present time, if the United States does not lead the
Soviet Union, it is only because (1) the United States does not have
large-scale test facilities and (2) the U.S. program never stressed
materials development. The United States may already be in the process
of taking the initiative away from the Soviets. Except for the Soviet
work with fiber-reinforced composites at IHT [9,13,77-79], the Soviets
in recent years have not shown any innovative approaches to MHD materials
problems, while U.S. researchers have proposed at least two new research
directions.

1.   Evaluation of coal slag as an electrode or protective-coating
material.

2.   Development of the composite hercynite/magnetite ($FeAl_2O_4$-
Fe_3O_4) electrode.

Coal-slag is believed by some U.S. specialists to be a most prom-
ising candidate material for electrodes in coal-fired systems. And,
where used as a protective coating, slag may permit the use of high
temperature alloys previously considered unacceptable. The hercynite/
magnetite electrode [3] may represent the solution of the multiple com-
patibility problems in MHD structures described earlier. Neither of
these materials, however, has yet to be adequately tested in an actual
MHD duct. Initial measurements of coal slag on cold copper at UTSI have
been favorable.

The study of complex oxynitride solid solutions for MHD high tempera-
ture applications, which has also been recently considered, represents the
search for totally new materials, whose final parameters (or even exist-
ence) cannot be predicted in advance. It may require several years
to learn to fabricate a single compound. Only one such material has as
yet been fabricated -- Sialon, a solid solution of silicon nitride and
alumina -- and only with great difficulties (and there has been some
question as to its quality). U.S. specialists, however, generally agree
with the supposition that there are probably very interesting compounds
in the Zr-Al-N-O and Zr-La-N-O systems.

In terms of MHD electrodes and insulators for coal-fired systems, the fundamental question is whether these materials will be stable against oxidation and corrosion. The oxidation and subsequent loss of material has been a major drawback with such very impressive compounds as ZrB_2, SiC, and Si_3N_4.

The corrosion resistance of the proposed materials should probably be as good as suggested by their proponents. However, the corrosion resistance of most pure, stable ceramics is good. It is the dirty, porous, commercial variety that behaves poorly. Some U.S. specialists believe that the *real innovation* will come when we learn how to stabilize or negate the impurities in commercial materials -- for example, by adding CaO to zirconia refractories to tie up the silicates at grain boundaries as calcium silicate and thereby increase the creep resistance.

Materials problems have long been singled out as one of the primary inhibiting factors preventing the ultimate development of commercial open-cycle MHD. However, the majority of all previous R&D efforts in MHD have been devoted to the demonstration of the engineering and fundamental feasibility of MHD systems (mainly in terms of generator development), and MHD materials research has been relatively neglected. According to some U.S. materials specialists, recent research suggests that the central question is not one of overcoming insurmountable materials barriers but of properly designing an R&D effort to address the MHD materials question in an orderly and consistent fashion [8].

The United States is expected to implement just such an MHD program in 1975. A recent draft proposal [8] for an overall program plan for the development of MHD power generation (open-cycle systems) has incorporated a significant materials R&D activity. This materials effort is also an integral part of every other program sub-element, so that a maximum benefit can be gained from all materials investigations.

Appendix

SOVIET INSTITUTES INVOLVED IN MATERIALS RESEARCH OR TESTING

All-Union Scientific Research Institute of Aviation Materials, Moscow
(Vsesoyuznyy nauchno-issledovatel'skiy institut aviatsionnykh materialov)

Institute on the Problems of Materials of the USSR Academy of Sciences
(Institut problem materialovedeniya)

Institute on the Physics of Metals of the USSR Academy of Sciences
(Institut metallofiziki)

Bauman Moscow Higher Technical School
(Moskovskoe vysshee tekhnicheskoe uchilishche im. N. E. Baumana)

Institute of High Temperatures of the USSR Academy of Sciences
(Institut vysokikh temperatur)

Institute of Polymer Mechanics of the Latvian SSR Academy of Sciences
(Institut mekhaniki polimerov)

Institute on Casting Problems of the USSR Academy of Sciences
(Institut problem lit'ya)

Kharkov Polytechnic Institute
(Khar'kov politekhnicheskiy institut)

Institute of Physical Chemistry of the USSR Academy of Sciences
(Institut khimicheskoy fiziki)

Baykov Institute of Metallurgy of the USSR Academy of Sciences
(Institut metallurgii im. A. A. Baykova)

Ukrainian Steel Scientific Research Institute
(UkrNIIspetsstal')

Ukrainian State Planning Institute of Nonferrous Metallurgy
(Ukrgiprotsvetmet)

Ukrainian Scientific Research Institute of Refractory and Acid-Resistant
Materials
(UkrIOK)

Ukrainian Scientific Research Institute of Refractories
(UkrNIIO)

Tomsk Polytechnic Institute
(Tomskiy politekhnicheskiy institut)

Dnepropetrovsk Metallurgical Institute
  (Dnepropetrovskiy metallurgicheskiy institut)

All-Union Scientific Research Institute
  (VNII)

Central Scientific Research Institute of Ferrous Metallurgy
  (TsNIIChERMET)

All-Union Scientific Research Institute of Refractory and Acid-
  Resistant Materials
  (VIOK)

All-Union Scientific Research Institute of Ceramics
  (VNIIK)

All-Union Scientific Research Institute of Refractories
  (VNIIO)

All-Union Scientific Research Institute of Glass
  (VNIIS)

All-Union Scientific Research Institute of Glass Fibers
  (VNIISV)

All-Union Scientific Research Institute of Glass Plastics
  and Glass Fibers
  (VNIISSV)

All-Union Scientific Institute of Hard Alloys
  (VNIITS)

All-Union Scientific Research Institute of Nonferrous Metallurgy
  (VNIITsvetmet)

All-Union Scientific Research Institute of Cements
  (VNITs)

State Scientific Research and Planning Institute of the Nitrogen
  Industry and Products of Organic Synthesis
  (GIAP)

State Scientific Research Institute of Ceramics
  (GIKI)

State Scientific Research Institute of Nonferrous Metals
  (GINTsVETMET)

State Scientific Research and Planning Institute of Alloys
  and Nonferrous Metal Processing
  (Giprotsvetmetobrabotka)

All-Union State Scientific Research and Planning Institute of the
  Cement Industry
  (Giprotsement)

State Scientific Research and Planning Institute of the Rare Metals Industry
  (GIRedmet)

State Scientific Research Institute of Glass
  (GIS)

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